Master's Thesis

Distribution of PCDD/Fs and PCBs in soils and pine needles in Ulsan, South Korea

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Abstract

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs), known as persistent organic pollutants, are unintentionally released from anthropogenic sources (incomplete combustion and formulation of commercial products). There have been no domestic studies such as widespread distribution of target compounds in bioindicator (pine needle) and indicator (soil) to be carried out. In this study, the spatial distribution and the contamination characteristics of PCDD/Fs and PCBs in terms of their regional features were investigated.

The soil and pine needle samples were collected at 30 sampling sites including suburban (S1−13), urban (U1−7), and industrial (I1−10) sites in Ulsan in December 2018. Soil and pine needle samples were extracted by Soxhlet extractor for 24 hours, and only pine needle samples were conducted with sulfuric acid treatment and filtered with bulk silica gel for removal of interfering substances. Then, soil and pine needle samples were cleaned up in multilayer silica gel columns. The target compounds were 17 PCDD/Fs and 18 PCBs (dioxin-like PCBs and indicator PCBs) analyzed by gas chromatography/high solution mass spectrometry (GC/HRMS). For interpreting the data, spatial distributions, compositions, and correlations of PCDD/Fs and PCBs in soils and pine needles were carried out.

The mean concentrations of PCDD/Fs, dioxin-like PCBs (dl-PCBs), and indicator PCBs in soils were 77.73, 90.11, 452.98 pg/g dw, respectively, and the mean concentrations of these compounds in pine needles were 6.26, 31.36, 166.37 pg/g ww, respectively. In general, industrial sites showed higher concentrations of PCDD/Fs and PCBs in soil samples than those in urban and suburban sites, indicating that industrial processes were mainly influenced the compounds in the industrial areas. However, there was no significant difference in PCDD/F and PCB levels between three sites in pine needles due to the long-range transport and unstable deposition state based on the physicochemical properties of organic pollutants.

The average composition of $\sum_7$PCDDs in soils accounted for about 77% of the normalized concentrations, whereas $\sum_{10}$PCDFs in pine needles were predominant about 82% of the normalized concentrations. Fractions of dl-PCBs and indicator PCBs in soils accounted for about 85%, 60% of penta- and hexa-CBs, respectively. In the case of pine needles, about 87% of tetra- and penta-CBs for dl-PCBs, about 80% of tri- to penta-CBs for indicator PCBs were accounted for the normalized concentrations, respectively. Based on the correlation results, PCDD/Fs and PCBs were positively correlated with each other. Total organic carbon content was significantly correlated with furans and heavy chlorinated PCBs, but lipid content had a negative or no correlation between any compounds.

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I. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) listed under Annex C by Stockholm Convention. Those compounds take measures of cutting down unintentional releases during the industrial processes, production of commercial products, and so on (UNEP, 2017). The molecular structures and nomenclature of PCDD/Fs and PCBs are shown in Figure 1. These compounds, consisting of planar aromatic structures with the number of chlorines, are usually persistent in that they prone to accumulate in the environmental media such as soil, sediment, and water over decades. PCDD/Fs have 210 congeners (75 PCDDs and 135 PCDFs) to be found, but isomers with chlorine(s) in the 2,3,7,8 positions are the most toxic substances when exposing to human beings and animals. Consequently, 17 congeners including 7 PCDDs and 10 PCDFs in reduced form are of common interest for POPs-related studies. They can be also divided into homologues (tetra- to octa-), the group(s) of congeners with same number of chlorines in different positions (Fueno et al., 2002; Rainer, 1998; Srogi, 2008). PCBs are comprised of 209 congeners with the number of chlorine atoms, and there are 12 coplanar PCBs called dioxin-like PCBs (dl-PCBs), which have the similar toxicity as PCDD/Fs. Among the non-dioxin-like congeners, seven indicator PCBs are the representative congeners to see the impacts of contamination of biota in the presence of massive amount of technical mixtures and in environmental matrices (Pereira, 2004).

PCDD/F and dl-PCB congeners have toxic effects on living organisms, and toxic equivalency factor (TEF) values were determined by binding tendency of its cytoplasmic receptor protein in accordance with their physicochemical properties and behaviors (Pereira, 2004; Srogi, 2008). Moreover, the octanol-air partition coefficient (K_{oa}) and octanol-water partition coefficient (K_{ow}) are the key physicochemical parameters for explaining the partition of PCDD/Fs and PCBs between water (and air) and environmental organic phases (Li et al., 2006). TEFs and calculated K_{ow} and K_{oa} values of individual congeners in logarithmic scale are listed in Table 1.

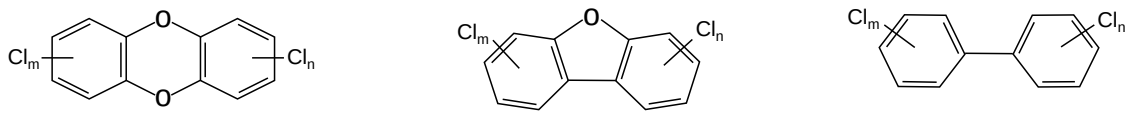

Figure 1. Molecular structures and nomenclature of PCDD, PCDF, and PCB.

Table 1. Toxic equivalent factors (TEF) from WHO, octanol-water (K_{ow}) and octanol-air (K_{oa}) partition coefficients of PCDD/F and dl-PCB congeners at 25 ºC (Log K_{oa} at 20 ºC is marked * as asterisk).

Class	Compound	TEF (1998)	TEF (2005)	Log K_{ow}	Log K_{oa}
Chlorinated dibenzofurans	2,3,7,8-TCDF	0.1	0.1	6.46[a]	9.42[b]
	1,2,3,7,8-PCDF	0.05	0.03	6.99[a]	10.1[b]
	2,3,4,7,8-PCDF	0.5	0.3	7.11[a]	10.09[b]
	1,2,3,4,7,8-HxCDF	0.1	0.1	7.53[a]	10.64[b]
	1,2,3,6,7,8-HxCDF	0.1	0.1	7.57[a]	10.68[b]
	2,3,4,6,7,8-HxCDF	0.1	0.1	7.76[a]	11.17[b]
	1,2,3,7,8,9-HxCDF	0.1	0.1	7.65[a]	10.79[b]
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	8.01[a]	11.25[b]
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	8.23[a]	11.62[b]
	OCDF	0.0001	0.0003	8.6[a]	12.1[b]
Chlorinated dibenzo-*p*-dioxins	2,3,7,8-TCDD	1	1	6.96[a]	10.14[b]
	1,2,3,7,8-PCDD	1	1	7.5[a]	10.72[b]
	1,2,3,4,7,8-HxCDD	0.1	0.1	7.94[a]	11.17[b]
	1,2,3,6,7,8-HxCDD	0.1	0.1	7.98[a]	11.21[b]
	1,2,3,7,8,9-HxCDD	0.1	0.1	-	11.35[c]
	1,2,3,4,6,7,8-HpCDD	0.01	0.01	8.4[a]	11.87[b]
	OCDD	0.0001	0.0003	8.75[a]	12.43[b]
Dioxin-like PCBs	PCB 77	0.0001	0.0001	6.025[d]	9.254[e]
	PCB 81	0.0001	0.0003	5.854[d]	-
	PCB 105	0.0001	0.00003	6.218[d]	9.633[e]
	PCB 114	0.0005	0.00003	6.218[d]	-
	PCB 118	0.0001	0.00003	6.404[d]	9.88[e*]
	PCB 123	0.0001	0.00003	6.404[d]	-
	PCB 126	0.1	0.1	6.404[d]	10.315[e*]
	PCB 156	0.0005	0.00003	6.991[d]	10.647[e*]
	PCB 157	0.0005	0.00003	6.991[d]	10.647[e*]
	PCB 167	0.00001	0.00003	6.991[d]	10.647[e*]
	PCB 169	0.01	0.03	6.991[d]	11.082[e*]
	PCB 189	0.0001	0.00003	7.359[d]	11.4141[e*]
Indicator PCBs	PCB 28	-	-	5.5[d]	8.346[e*]
	PCB 52	-	-	6.025[d]	8.518[e]
	PCB 101	-	-	6.404[d]	9.265[e]
	PCB 138	-	-	6.988[d]	10.212[e*]
	PCB 153	-	-	6.991[d]	10.012[e]
	PCB 180	-	-	7.359[d]	10.759[e]

a - Govers et al., 1998, b - Chun, 2015, c - Moussaoui et al., 2012, d - Paasivirta et al., 2009, e - Li et al., 2006; PCB 118 is also included in indicator PCBs (marked as bold text).

The main sources of PCDD/Fs are incomplete combustion and thermal processes from waste incineration (Yu et al., 2006), and those anthropogenic sources like herbicide industries (Moussaoui et al., 2012), chlorine and paper industries (Zheng et al., 2001), melting processes (Pham et al., 2019) and car traffics (Kim et al., 2003) are inevitable to emit PCDD/Fs as well (Pereira, 2004; Watanabe et al., 1999). Once they are emitted from the sources (usually combustions), adsorption in dust or soot particles happens, which finally leads to the depositions on soil, water, and even vegetation. Consequently, it would lead to human exposure from the dietary intake or drinking, thereby carcinogenicity and mortality of premature infant would increase (Srogi, 2008).

Polychlorinated biphenyls, especially indicator PCBs, can be produced as many commercial mixtures named Aroclor in USA, Clophen in Germany, Phenoclor in France, Fenclor in Italy, and Kanechlor in Japan since the 1920s, and they were used as coatings, inks, flame retardants, and paints. Even though the usage of technical mixtures had been banned for several countries in the 1970s owing to their toxicity through biomagnification, their application in a closed system such as capacitors and transformer oil are in use for the present days (Frame et al., 1996; Pereira, 2004). Dioxin-like PCBs are literally as toxic as PCDD/Fs, and therefore, they were formed from the municipal solid waste incineration as a byproduct (Sakai et al., 2001) released from commercial PCB formulations (Alcock et al., 1998; Tiernan et al., 1983). PCBs also have similar pathways of PCDD/Fs, which would be polluted to the environment, disrupting the food chain system (Nieuwoudt et al., 2009).

Most studies were well conducted to evaluate the behavior of POPs in soils or sediments as a representative environmental medium to determine regional characteristics (industrial, urban, or suburban), or to determine whether the pollutant concentration level exceeded the emission standards of water or air (Loganathan et al., 2008). Since 2001, pine-related studies had been exponentially increased until now, whereas soil-related studies had been steadily increased. Moreover, few studies about POPs with more than one medium were also performed per year (Figure 2). Among the studies in South Korea, the levels of persistent organic pollutants in animal and plant products including human risk assessments had been observed and evaluated through dietary intake and dermal contact (Chung et al., 2018). Moreover, domestic studies have dealt with part of the ecosystem by identifying the sources or patterns of organic pollutants from the water, soil/sediment, and passive sampler. However, it is rare to see the monitoring studies with two or more mediums (especially bioindicators) to see the spatial trend of certain places in Korea. The objective of this study is to understand the behaviors and multimedia fate of organic pollutants by investigating the spatial distributions and identifying the sources of organic pollutants in two different media: soil and pine needle.

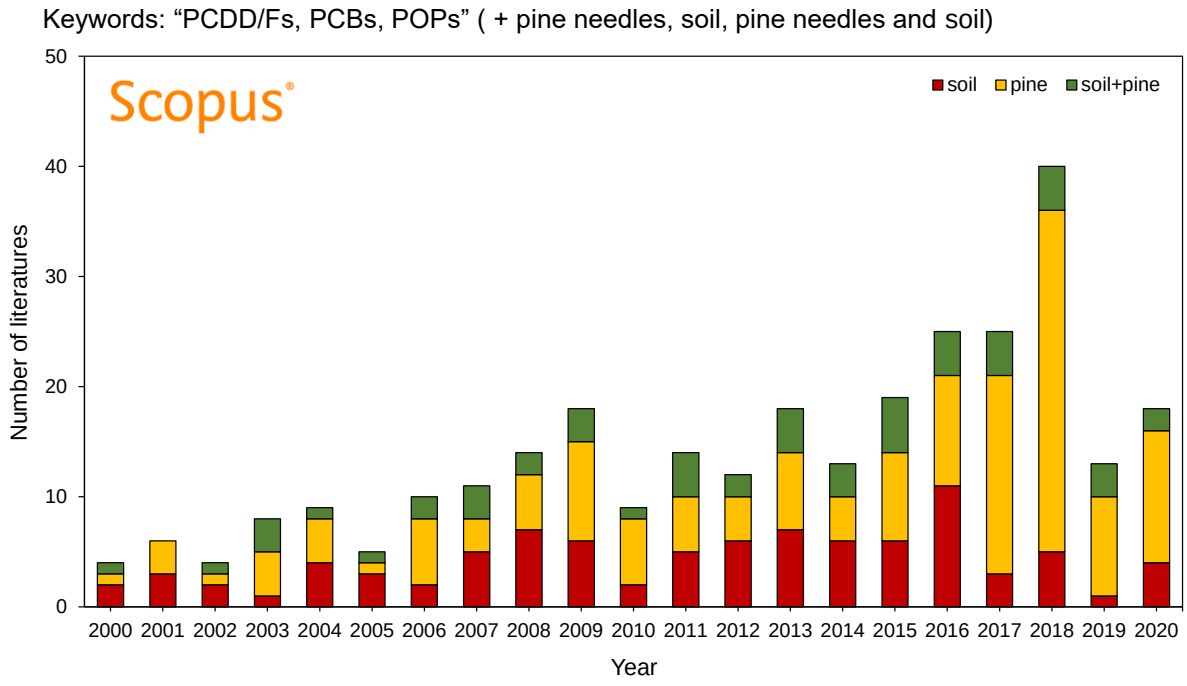

Figure 2. Temporal trend of POPs-related studies in soils and pine needles.

II. MATERIALS AND METHODS

2.1 Sampling methods

Soil and pine needle samples were collected in Ulsan between December 7−19, 2018. A total of 30 sampling sites were categorized into three groups: suburban (S1−13), urban (U1−7), and industrial (I1−10) sites (Figure 3). In order to collect both soil and pine needle samples, pine trees were selected considering the locations of sampling sites. Sub-soil (5 cm under the topsoil layer) within a radius of 1 meter from the selected pine tree was collected with a hand shovel, and then stored in plastic bags at −4 ºC. About 10 g of soil samples were dried at room temperature inside the hood for few days and homogenized after the removal of debris and gravels using a 2 mm mesh sieve. One-year-old pine needles with bud shoots were collected by using pruning shears at each sampling site. They were wrapped in aluminum foil and stored in the plastic bags without oxygen at the same temperature as soil samples. About 10 g of pine needle samples were brushed for debris removal and cut into 3−5 cm by cleaned stainless steel scissors.

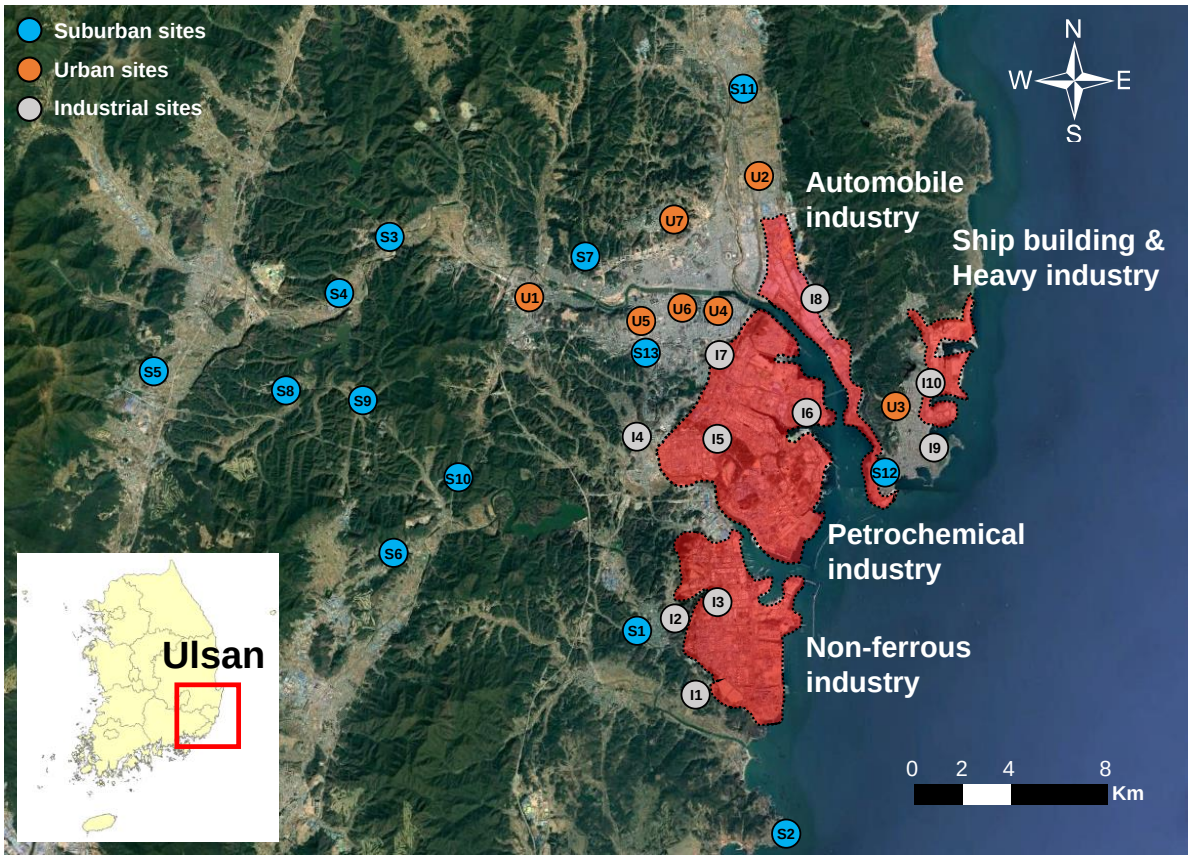

Figure 3. Locations of sampling sites, which are categorized into suburban, urban, and industrial areas in Ulsan, South Korea.

2.2 Pretreatment procedures

Ten grams of soil and pine needle samples were added with anhydrous sodium sulfate for dehydration and Soxhlet-extracted overnight using 350 mL dichloromethane (DCM) and 350 mL hexane: acetone (3:1), respectively. Surrogate standards (EPA-1613LCS, EPA-1668LCS) were spiked into each sample before the extraction. The solvent exchange (DCM to hexane) was done using a rotary evaporator. Before the clean-up, sulfuric acid treatment and filtration using activated silica gel were performed only for pine needle samples for the removal of interfering substances such as chlorophyll and organic species (Loganathan et al., 2008; Ok et al., 2002). Both soil and pine needle extracts were cleaned up with multi-layer silica gel columns (From the top, 3 g anhydrous sodium sulfate, 3 g 10% $AgNO_3$-silica gel, 1 g activated silica gel, 4.5 g 22% H_2SO_4-silica gel, 4.5 g 44% H_2SO_4-silica gel, 1 g activated silica gel, 2 g 2% KOH-silica gel, 1 g activated silica gel, and 1 g anhydrous sodium sulfate). The extracts were eluted with 150 mL hexane after loading into the columns. The samples were concentrated to 50 µL and internal standards (EPA-1613ISS, EPA-1668ISS) were spiked into the vials (Figure 4).

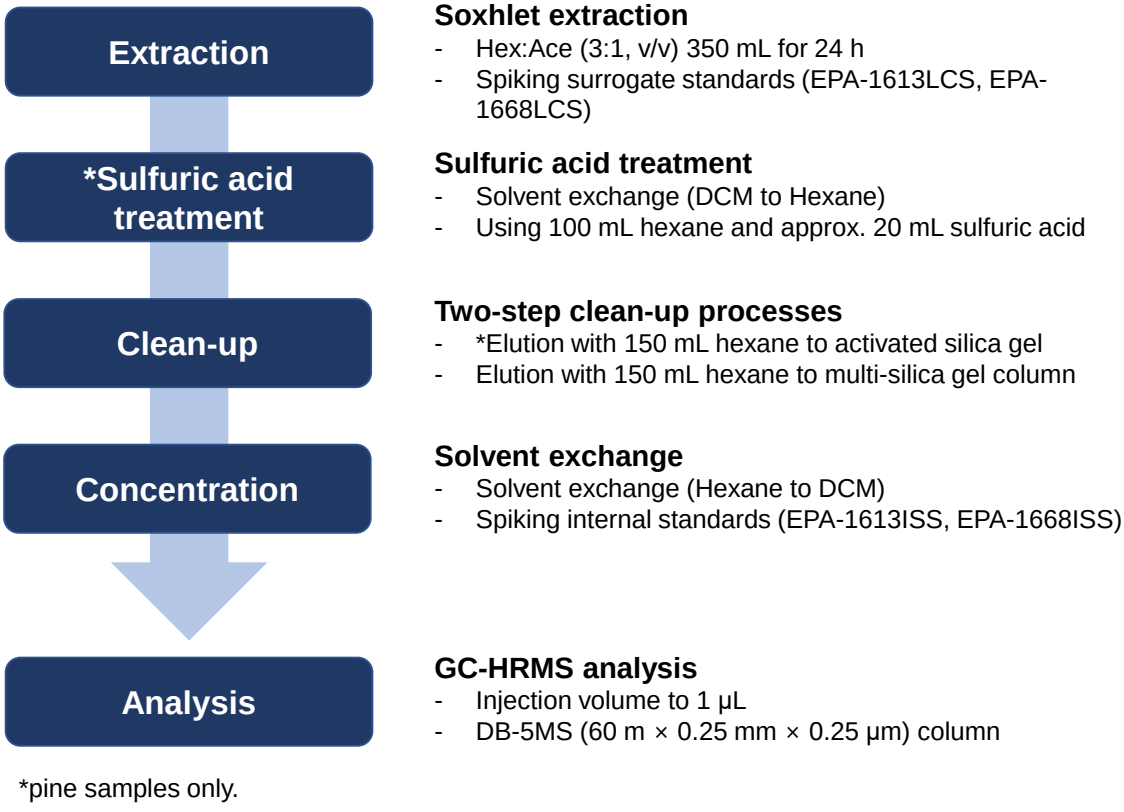

Figure 4. Clean-up procedures for soils and pine needles prior to instrumental analysis.

2.3 Instrumental analysis

Target compounds including PCDD/Fs and PCBs (dl-PCBs and indicator PCBs) were analyzed by gas chromatograph (GC, Agilent 7980A, USA) coupled with a high-resolution mass spectrometer (HRMS, Auto Spec Premier, Waters, USA) (Figure 5). Table 2 summarizes the instrumental conditions for analysis of PCDD/Fs and PCBs.

Table 2. Instrumental conditions of GC/HRMS.

	PCDD/Fs	**PCBs**
Injection temperature	320 ℃	300 ℃
Injection mode	Splitless	Splitless
Carrier gas	He	He
Column	DB-5MS (60 m x 0.25 mm x 0.25 μm thickness)	DB-5MS (60 m x 0.25 mm x 0.25 μm thickness)
Oven	100 ℃ (1 min) → 20 ℃/min → 200 ℃ → 2.5 ℃/min → 300 ℃ → 10 ℃/min → 340 ℃ (2 min)	90 ℃ (1 min) → 20 ℃/min → 170 ℃ (4 min) → 3.5 ℃/min → 280 ℃ → 50 ℃/min → 320 ℃ (5.77 min)
Mode	EI/SIM	EI/SIM

Figure 5. Gas chromatograph (GC, Agilent 7980A, USA) coupled with a high-resolution mass spectrometer (HRMS, Auto Spec Premier, Waters, USA).

2.4 Quality assurance and quality control

The average recoveries of the PCDD/Fs and PCBs were 91.2%, 100.2% in soils, and 93.2, 109.7% in pine needles, respectively. Procedural blanks were conducted for laboratory contamination through the entire analytical processes (Loganathan et al., 2008). The instrumental detection limit (IDL) values and standard deviations were calculated from the values where the lowest calibration standards of the target compounds for seven times were analyzed. The limit of quantification (LOQ) was determined at signal-to-ratio (S/N) of 10. All sample peaks were identified by retention time compared to standards if signal-to-noise ratio was over 3 (Table 3 and 4).

Table 3. The values of the instrumental detection limit (IDL) and the limit of quantification (LOQ) for PCDD/Fs.

Compound (pg)	IDL 1	IDL 2	IDL 3	IDL 4	IDL 5	IDL 6	IDL 7	SD	IDL	LOQ
2378-TCDF	0.250	0.247	0.255	0.233	0.249	0.236	0.260	0.010	0.031	0.098
12378-PeCDF	1.263	1.235	1.249	1.249	1.261	1.246	1.262	0.010	0.032	0.103
23478-PeCDF	1.259	1.225	1.288	1.245	1.270	1.207	1.248	0.027	0.085	0.272
123478-HxCDF	1.277	1.217	1.265	1.238	1.278	1.213	1.225	0.028	0.088	0.282
123678-HxCDF	1.262	1.253	1.253	1.240	1.257	1.242	1.258	0.008	0.026	0.081
234678-HxCDF	1.240	1.280	1.218	1.304	1.239	1.255	1.234	0.030	0.093	0.296
123789-HxCDF	1.218	1.229	1.306	1.216	1.257	1.239	1.233	0.031	0.098	0.312
1234678-HpCDF	1.234	1.236	1.243	1.244	1.221	1.275	1.266	0.019	0.059	0.188
1234789-HpCDF	1.289	1.307	1.270	1.228	1.222	1.191	1.232	0.041	0.130	0.414
OCDF	2.498	2.508	2.506	2.499	2.496	2.502	2.503	0.005	0.014	0.045
2378-TCDD	0.252	0.258	0.239	0.257	0.246	0.245	0.283	0.014	0.045	0.144
12378-PeCDD	1.239	1.274	1.271	1.288	1.202	1.195	1.256	0.036	0.113	0.361
123478-HxCDD	1.221	1.268	1.273	1.222	1.273	1.235	1.286	0.027	0.085	0.271
123678-HxCDD	1.289	1.276	1.255	1.266	1.238	1.240	1.264	0.019	0.059	0.187
123789-HxCDD	1.219	1.286	1.283	1.272	1.206	1.187	1.286	0.043	0.135	0.431
1234678-HpCDD	1.277	1.269	1.276	1.247	1.290	1.254	1.258	0.015	0.047	0.151
OCDD	2.497	2.521	2.494	2.562	2.523	2.452	2.528	0.034	0.108	0.343

Table 4. The values of the instrumental detection limit (IDL) and the limit of quantification (LOQ) for PCBs.

Compound (pg)	IDL 1	IDL 2	IDL 3	IDL 4	IDL 5	IDL 6	IDL 7	SD	IDL	LOQ
PCB 77	0.216	0.193	0.199	0.182	0.204	0.192	0.199	0.011	0.033	0.105
PCB 81	0.204	0.218	0.202	0.190	0.204	0.213	0.190	0.011	0.033	0.105
PCB 105	0.196	0.201	0.175	0.218	0.190	0.221	0.210	0.016	0.051	0.162
PCB 114	0.197	0.221	0.207	0.212	0.208	0.174	0.180	0.017	0.054	0.172
PCB 118	0.223	0.234	0.212	0.168	0.179	0.175	0.178	0.027	0.084	0.268
PCB 123	0.193	0.241	0.211	0.220	0.197	0.188	0.177	0.022	0.069	0.218
PCB 126	0.188	0.202	0.198	0.173	0.251	0.164	0.251	0.035	0.110	0.349
PCB 156	0.200	0.182	0.211	0.174	0.216	0.217	0.198	0.017	0.052	0.166
PCB 157	0.203	0.204	0.202	0.218	0.195	0.196	0.211	0.008	0.026	0.082
PCB 167	0.187	0.197	0.178	0.217	0.224	0.183	0.220	0.019	0.061	0.194
PCB 169	0.240	0.201	0.233	0.210	0.166	0.213	0.185	0.026	0.081	0.259
PCB 189	0.192	0.188	0.211	0.194	0.204	0.225	0.187	0.014	0.044	0.140
PCB 28	20.358	20.080	20.836	19.079	18.808	21.053	20.073	0.837	2.629	8.372
PCB 52	20.172	20.223	20.118	20.048	19.274	20.448	19.860	0.374	1.175	3.742
PCB 101	20.693	19.974	20.034	20.529	19.586	19.537	19.827	0.442	1.388	4.421
PCB 138	20.115	19.991	21.043	19.532	19.392	20.742	20.209	0.596	1.873	5.965
PCB 153	19.720	20.248	21.239	19.780	19.423	20.054	20.821	0.645	2.026	6.453
PCB 180	19.619	20.435	20.491	20.499	19.299	20.435	20.129	0.484	1.520	4.841

2.5 Lipid content and TOC

2.5.1 Lipid content in pine needles

The lipid content of the medium was measured for the correlation between organic pollutant levels and lipid content in each sample. An empty round flask was weighed before adding the extraction solvent. After the extraction, concentration was performed with the rotary evaporator until there was no solvent left in the flask. The lipid content was calculated by subtracting the weight of the flask after and before the extraction.

2.5.2 Total organic carbon content in soils

The total organic carbon (TOC) of soil was needed for comparing the contribution of organic carbons in each soil sample. TOC was determined by subtraction of total carbon (TC) and inorganic carbon (IC) contents using the TOC analyzer (TOC-L CPH, TOC-5000, Shimadzu, Japan) (Figure 6). The conditions of analytical instrument are shown in Table 5.

TOC (total organic carbon) = TC – IC

Table 5. Instrumental conditions of TOC analyzer.

	Temperature (℃)
TC (total carbon)	680 ℃
IC (inorganic carbon)	900 ℃
Supply gas	O_2
Carrier gas	Air

Figure 6. TOC analyzer (TOC-L CPH, TOC-5000, Shimadzu, Japan).

2.6 Statistical Analysis

A Mann-Whitney rank sum test was conducted to analyze the statistical differences between three distinctive areas (suburban, urban, and industrial) using SigmaPlot software 12.0. Principal component analysis (PCA) and Spearman correlation analysis were carried out by using IBM SPSS Statistics 20. PCA was used to figure out the possible sources from the multivariate components of target compounds in the samples, and Spearmen correlation analysis was used to examine the relationships between the PCDD/F and PCB levels, TOC content in soils, and lipid content in pine needles.

III. RESULTS AND DISCUSSION

3.1 Distribution of PCDD/Fs in soils and pine needles

3.1.1 Total concentrations of PCDD/Fs

A summary of the PCDD/F concentrations in soils and pine needles for all sites is shown in Figure 7. The concentrations of $\sum_{17}$PCDD/Fs in soils ranged between 8.83−237.96 pg/g dw (mean: 77.73 pg/g dw), with the highest values being detected near the industrial areas (Figure 7a). Industrial sites were statistically different from both suburban ($p < 0.001$) and urban ($p < 0.01$) sites, and this finding was supported by similar trends in the previous studies (Schuhmacher et al., 2004; Wu et al., 2018). In Ulsan, there are two well-known industrial complexes called Mipo national industrial complex (automobile, shipbuilding, and petrochemical) and Onsan national industrial complex (non-ferrous metals), while petroleum refining industries are located at both complexes (Choi et al., 2012). Therefore, it is not surprising that the samples from industrial areas are more polluted compared to those from urban and suburban areas. Moreover, when comparing the sum of 17 PCDD/Fs levels in soils from suburban and urban areas, the dioxin levels from suburban areas were a bit higher than those from urban areas, supporting the idea that suburban sites might be affected either from the local sources or from the urban and industrial sites (Nguyen et al., 2016).

The total 17 PCDD/F concentrations ranged between 1.22−36.39 pg/g ww (mean: 6.26 pg/g ww) in pine needles, and some sites located inside the industries such as I3 and I6 had the highest value of PCDD/Fs among the 30 sampling sites (Figure 7b). With respect to the pine needle samples, all three areas were not statistically different from each other (Mann-Whitney rank sum test, $p > 0.05$). According to a previous study, PCDD/F levels in chard sample from a control area were higher than those found in samples taken in the industrial area, but no significant difference was found due to the long-range transport of PCDD/Fs from meteorological conditions such as rainfall, wind directions and so on (Schuhmacher et al., 2004).

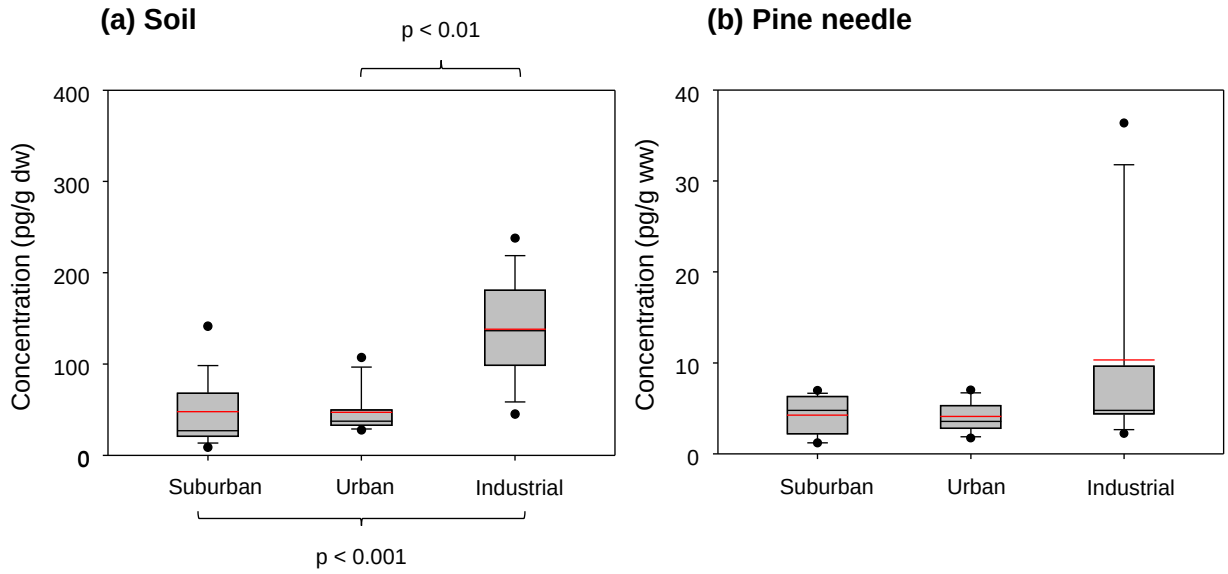

Figure 7. Box plots of $\sum_{17}$PCDD/F concentrations in two media in Ulsan, Korea.

3.1.2 Spatial distribution of PCDD/Fs

The spatial distributions of total PCDD/F levels in soils and pine needles at 30 sampling sites are displayed in Figure 8 using ArcGIS 10.5. Industrial sites generally showed higher concentrations of PCDD/Fs than suburban and urban sites for both media. The patterns of some sampling sites appear to be different.

Stacked bar graphs of PCDD/F homologues in concentrations at all sites are shown in Figure 9. In Figure 9a, most of the industrial sites show higher concentrations of PCDD/Fs in soils than those of other areas, and this result is consistent with those in previous studies (Dömötörová et al., 2012; Nieuwoudt et al., 2009; Wu et al., 2018), but some suburban sites (S9 to 12) had comparable PCDD/F levels to industrial sites, meaning that those sites may be polluted from local sources such as agricultural wood fires or traffic events (Schuhmacher et al., 2004).

In Figure 9b, the patterns of PCDD/Fs in pine needles among the sampling sites were somewhat similar except for two industrial sites (I3 and I6) with relatively high concentrations of PCDD/Fs. Those sites were influenced by the places where industrial complexes were directly located. The fractions of PCDD/F homologues in pine needles, on the other hand, were more diverse than those in soils, and therefore, their variations were not severe; when comparing the graphs of the two media, HxCDFs and HpCDFs in pine needles were more likely observed whereas OCDDs were widely distributed in soils.

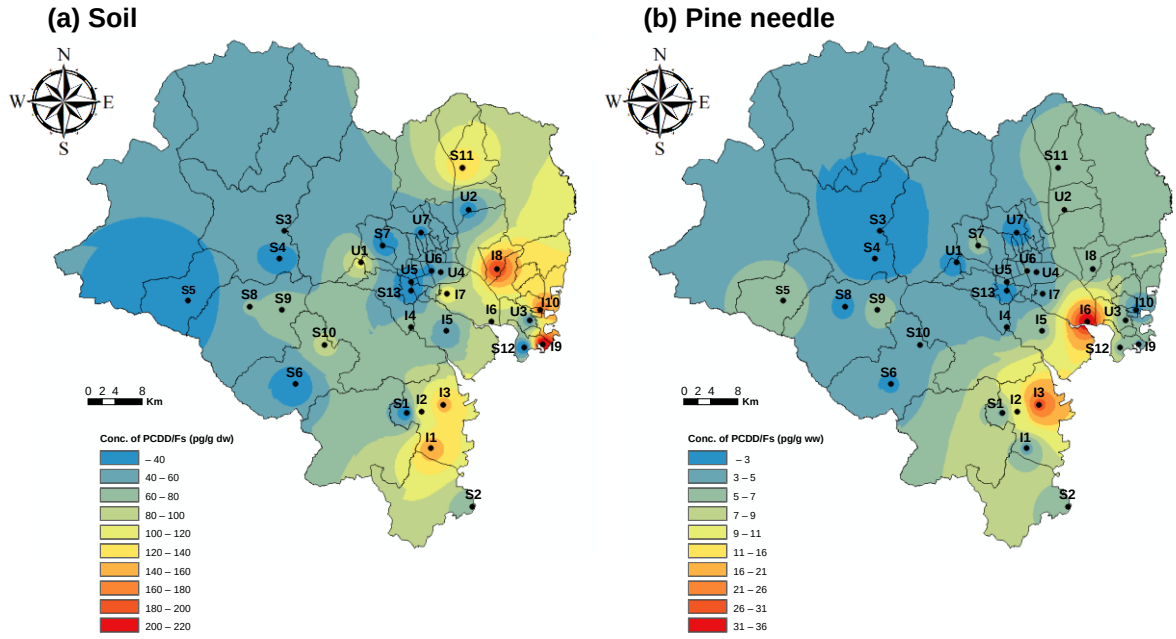

Figure 8. Contour maps of $\sum_{17}$PCDD/F concentrations in two media in Ulsan, Korea.

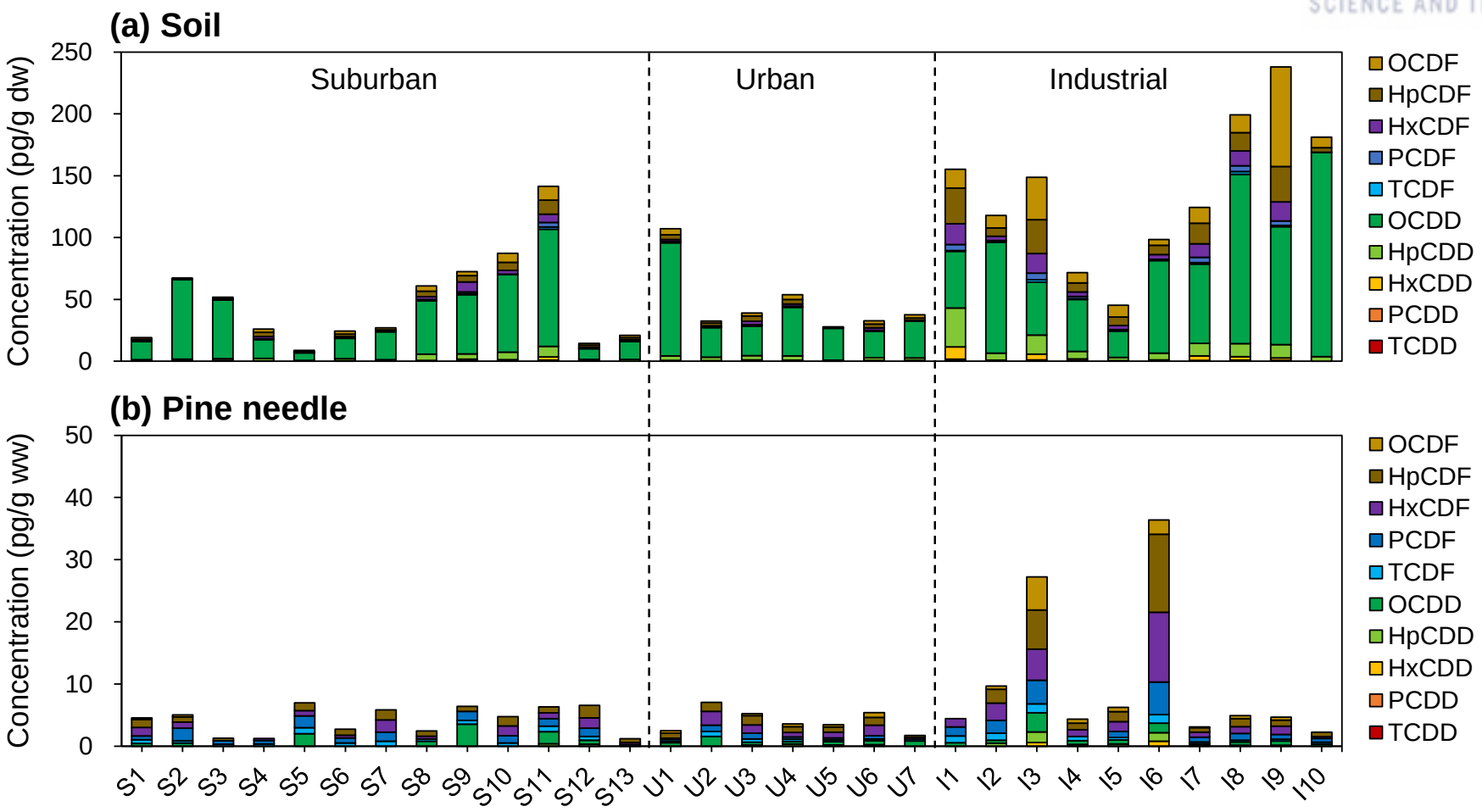

Figure 9. Levels of $\sum_{17}$PCDD/Fs in two media in Ulsan, Korea.

3.1.3 Average and individual profiles of PCDD/Fs

The average and individual profiles of the PCDD/F homologues for the three areas and each sampling site are illustrated in Figure 10 and 11, respectively. In Figure 10a, the average composition of $\sum_7$PCDDs accounted for about 77% of the normalized concentrations in soils. The industrial area had a different profile compared to those of the urban and suburban areas, contributing slightly higher $\sum_{10}$PCDFs due to the industrial activities. Similar trends were found in previous studies in China and Spain (Schuhmacher et al., 2004; Zhang et al., 2009).

In Figure 10b, the distribution patterns in pine needles are different from those of soils. The overall amount of PCDFs in the three areas was much larger than that of PCDDs (82%). Furans with higher contents of chlorines, such as HxCDFs and HpCDFs, were the predominant homologues for normalized concentrations in pine needles. The congeners in pine needles, such as 1,2,3,4,7,8-HxCDFs, 1,2,3,6,7,8-HxCDFs and 1,2,3,4,6,7,8-HpCDFs, contributed to these homologues, which was in accordance with PCDD/F distributions near the municipal incinerator and around the bay in previous studies (Hanari et al., 2004; Kim et al., 2005). This result might be mainly attributed to incomplete combustion as the ratio of $\sum_{10}$PCDFs to $\sum_7$PCDDs is greater than one (Chen et al., 2012).

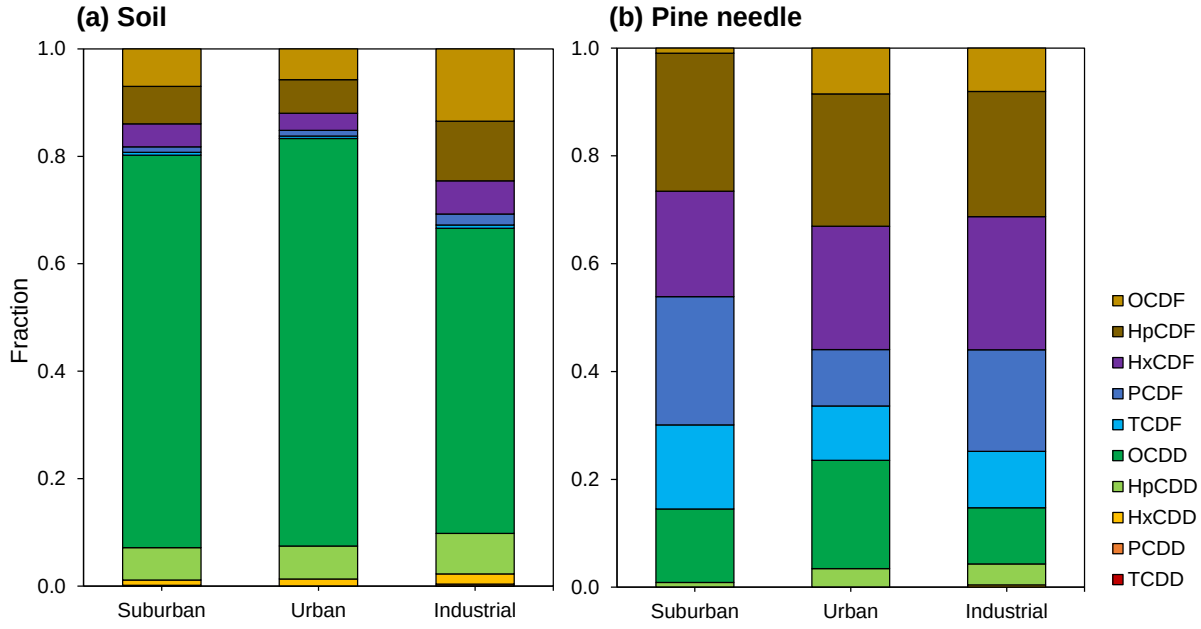

Figure 10. Average homologue profiles of PCDD/Fs in two media in Ulsan, Korea.

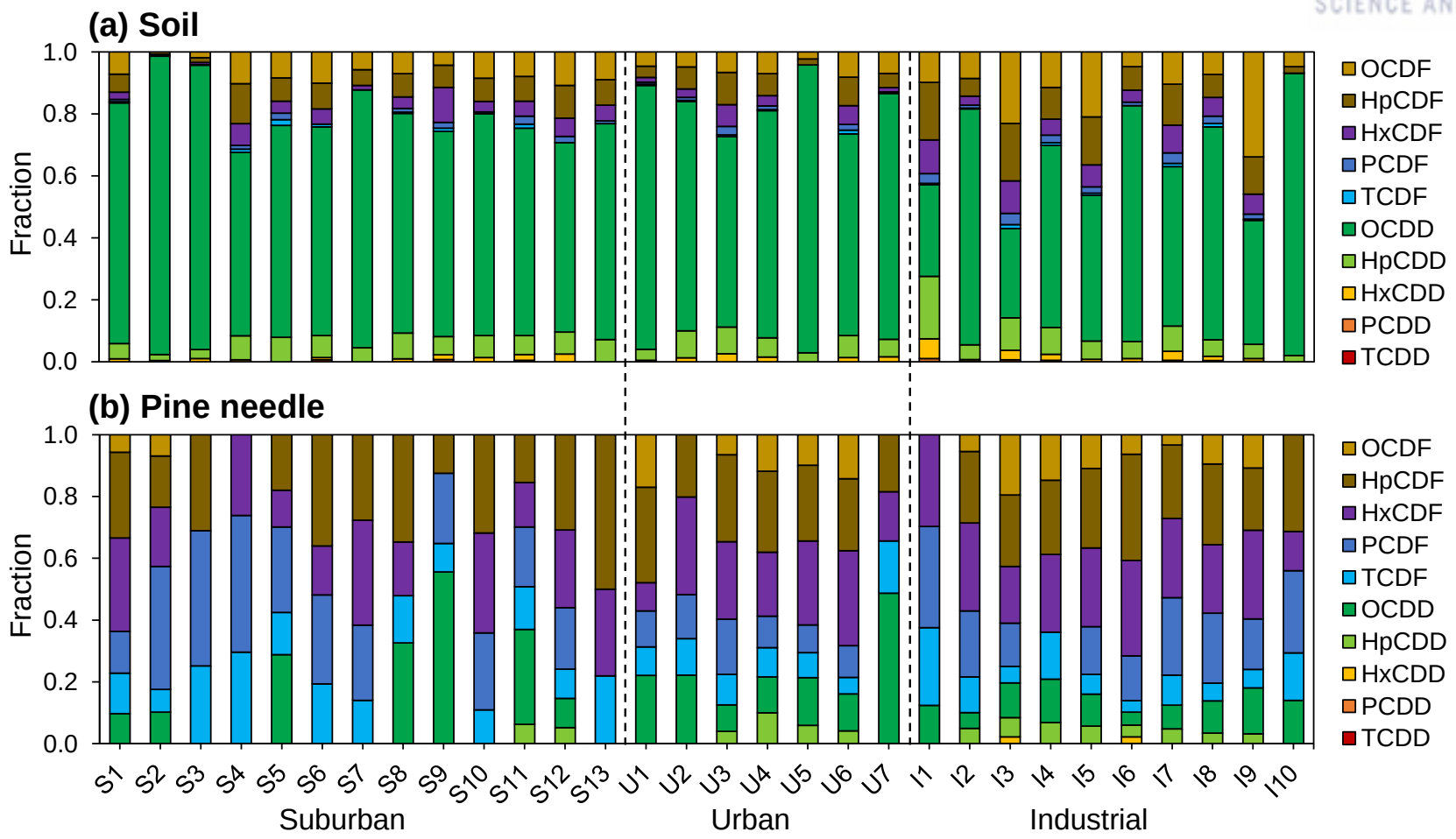

Figure 11. Individual homologue profiles of PCDD/Fs in two media in Ulsan, Korea.

3.1.4 Principal component analysis of PCDD/Fs

The purpose of PCA is to characterize pollution patterns from the various industrial and other (regional or local) sources from the sampling sites (Cho et al., 2019). Instead of using the PCDD/F homologue groups to conduct the PCA, PCDD/F congeners were used due to the better interpretations between loading and score plots.

The PCA score and loading plots for PCDD/Fs in the soils from the sampling sites are shown in Figure 12. In the loading plot, the principal components 1 (PC 1), accounting for 63% of the total variance, have positive loadings of almost all the PCDD and PCDF congeners, and negative loadings of some congeners (OCDF, 2,3,7,8-TCDF), whereas PC 2 (13%) was influenced by OCDD. In the score plot, a total of 30 samples were located based on their PCDD/F congener profiles. Some suburban samples were located between urban and industrial samples, assuming that they were affected by PCDD/F emission sources from both areas. Moreover, most of the sampling sites primarily correlated with OCDDs, one of the predominant congeners accumulated mainly in soils. In particular, higher chlorinated dioxins like OCDD can be formed through natural processes such as biomass burning, and therefore, most suburban sites had high fractions of OCDDs (Breivik et al., 2004). Among the industrial sites, I3, located on the outlier in the score plot (X-axis: -1.34, Y-axis: 3.73), positively correlated with OCDFs. It is assumed that the production of copper and aluminum through the rolling and pressing processes was the main source from the nonferrous industries (Antunes et al., 2012; Seo et al., 2011). Some suburban sites, such as S1 (X: 4.27, Y: 0.34), S6 and S8, were scattered in the score plot, meaning that they might be affected by the other local sources (mainly burning of woods and wastes).

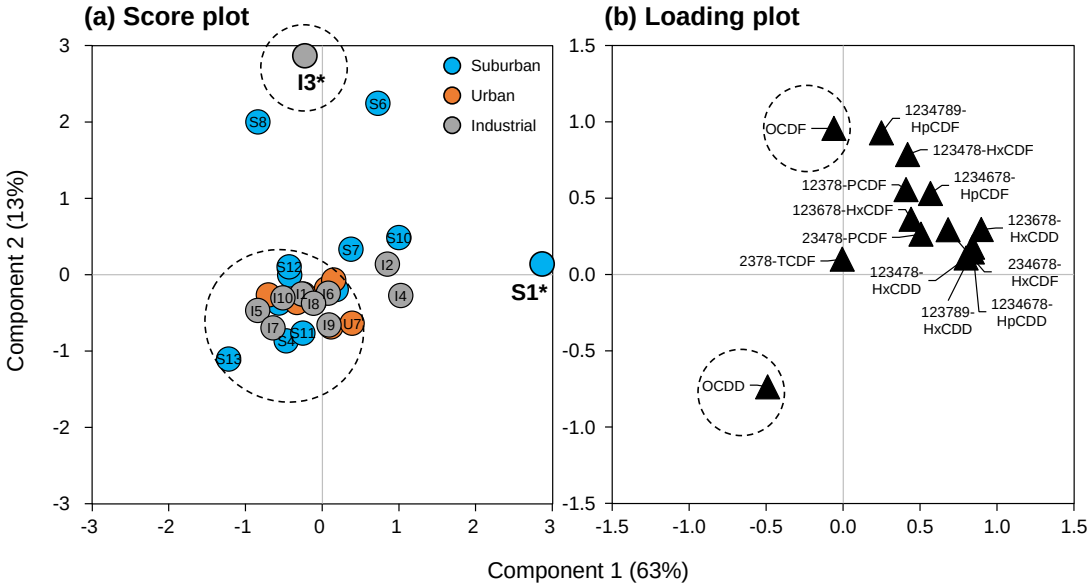

Figure 12. Principal component analysis results of PCDD/Fs in soils (**I3**, X: -1.34, Y: 3.73; **S1**, X: 4.27, Y: 0.34). 2,3,7,8-TCDD, 1,2,3,7,8,9-HxCDF, and 1,2,3,7,8-PCDD were excluded due to their detection rate less than 50%.

The three-dimensional scatter plots for the three principal components in pine needles from the sampling sites are shown in Figure 13. The first, second, and third principal components (X: PC 1, Y: PC 2, Z: PC 3) accounted for 30%, 19%, and 17% of the total variance, respectively. In the score plot, samples from industrial and urban sites were clustered with high loadings of specific congeners (2,3,7,8-TCDF, 1,2,3,7,8-PCDF, 2,3,4,7,8-PCDF, and 1,2,3,4,7,8-HxCDF). It is assumed that urban sites were mainly influenced by industrial processes through long-range transport, which can play an important role in the environmental levels of these pollutants (Schuhmacher et al., 2004). Samples from suburban sites were more scattered in the score plot when compared to those from other areas. The pine needle samples from S9 and U7 were characterized by OCDD with negative loading of PC 3. In this case, they were possibly polluted by the historical use of pesticides for agricultural activities or by illegal burning (Bochentin et al., 2007). The previous studies reported that pesticide products containing pentachlorophenol (PCP) for agricultural activities have been banned in South Korea since the 1970s, and therefore, their influence on high fractions of OCDDs is less likely (Masunaga et al., 2001).

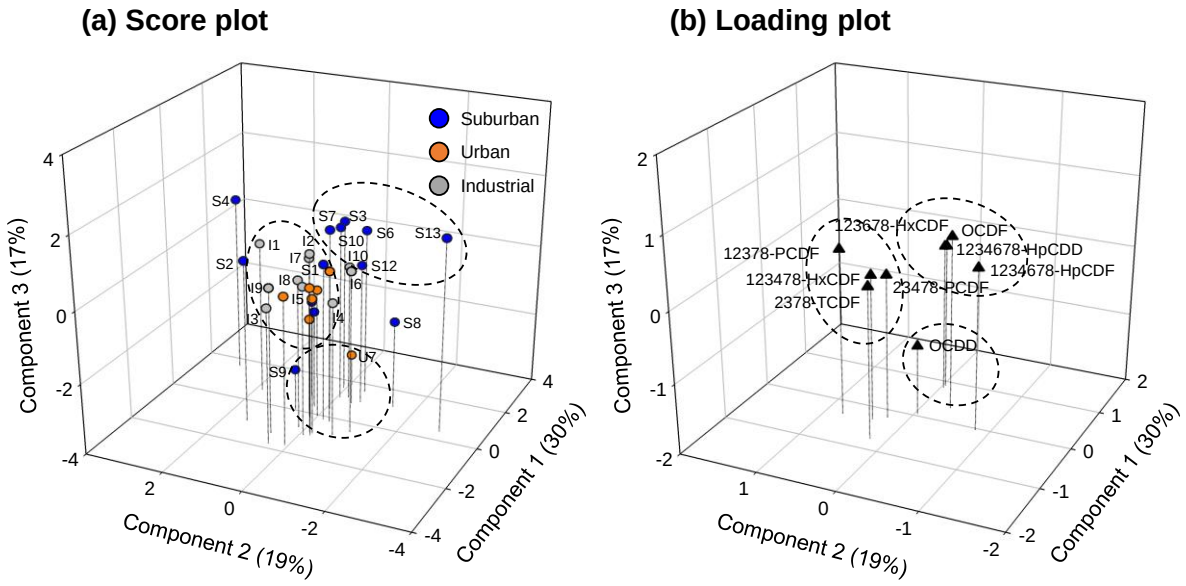

Figure 13. Principal component analysis results of PCDD/Fs in pine needles.

3.2 Distribution of dl-PCBs in soils and pine needles

3.2.1 Total concentrations of dl-PCBs

A summary of the dioxin-like PCB (dl-PCB) concentrations in soils and pine needles for all sites is shown in Figure 14. In Figure 14a, the concentrations of $\sum_{12}$PCBs in soils ranged between 7.90−470.73 pg/g dw (mean: 90.11 pg/g dw), and the dl-PCB levels from the industrial sites were about 4 times higher than those from the suburban and urban sites (Mann-Whitney rank sum test, $p < 0.01$). This can be explained for the same reasons as mentioned in the PCDD/F session, suggesting that industrial processes have been attributed to the dl-PCB emissions for a long period.

The total dl-PCB concentrations ranged between 14.66−65.09 pg/g ww (mean: 31.36 pg/g ww) in pine needles (Figure 14b). Unlike the tendency of PCDD/Fs in the same media, mean concentrations of dl-PCBs from industrial sites (33.13 pg/g ww) were comparable to those from urban and suburban sites (28.97−31.05 pg/g ww), giving no significant difference ($p > 0.05$). This result may not support the previous studies, in which dl-PCB levels from industrial sites and urban sites are much higher than those from remote sites (Holt et al., 2016). However, this could happen because the surroundings from the sampling sites can underestimate the levels of air pollution, considering that it may interfere with deposition in pine needles (Chung et al., 2018).

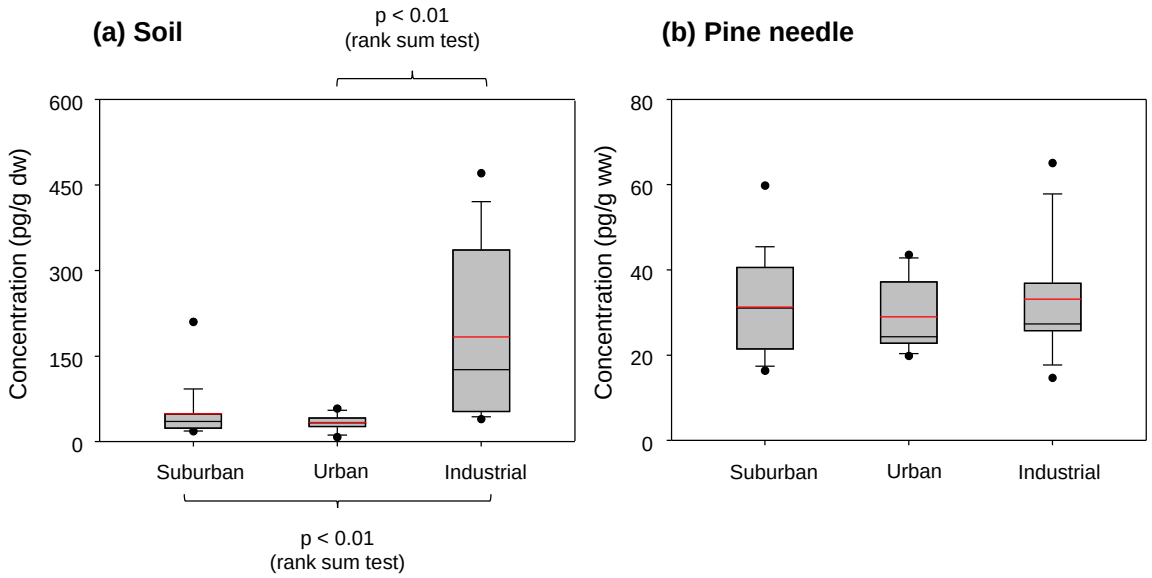

Figure 14. Box plots of $\sum_{12}$PCBs in two media in Ulsan, Korea.

3.2.2 Spatial distribution of dl-PCBs

The spatial distributions of total dioxin-like PCB levels in soil and pine needle samples are displayed in Figure 15. In general, the industrial areas were shown higher concentrations of dl-PCBs in soils than those from suburban and urban areas. Industrial sites (I7 and I8) were having the higher concentrations because of the area where petrochemical and automobile industries are located, whereas sites like dl-PCB levels in I2 and I3 were relatively low as those sites were located near the non-ferrous industries.

The stacked bar graphs of dl-PCB congeners in concentrations at all sites are shown in Figure 16. In Figure 16a, some industrial sites showed higher concentrations of dl-PCBs in soils than those of other areas, which is similar to those of PCDD/Fs in soils. Of the sampling sites, soil in the suburban site (S11) had the highest concentration of dl-PCBs similar to those of industrial sites. Since the sampling site is located between residential and agricultural areas, PCBs may show a local persistence in the vicinity of former production, storage, or use of technical mixture such as transformer oil (Schrenk et al., 2013).

In Figure 16b, the patterns of dl-PCBs in pine needles at sampling sites were similar except for one industrial area (I3) with higher concentration of dl-PCBs, assuming there were thermal processes to have occurred from the non-ferrous industries (Antunes et al., 2012). When comparing the graphs of the two media, PCB 118 and PCB 123 in pine needles were more likely observed whereas PCB 118 and PCB 105 were distributed in soils.

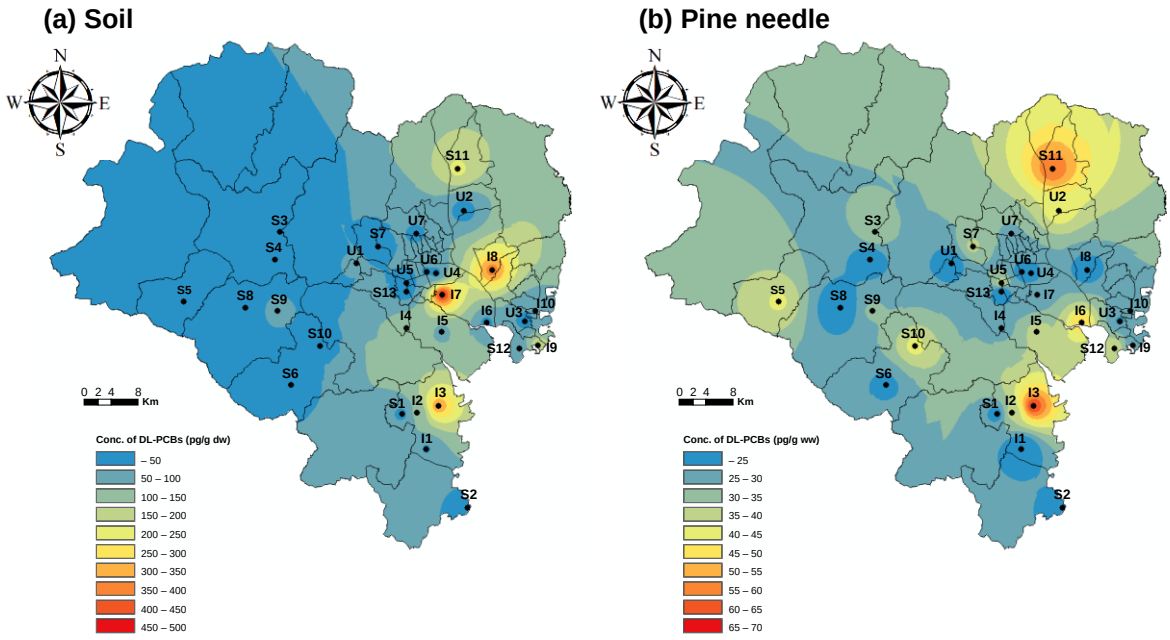

Figure 15. Contour maps $\sum_{12}$PCBs in two media in Ulsan, Korea.

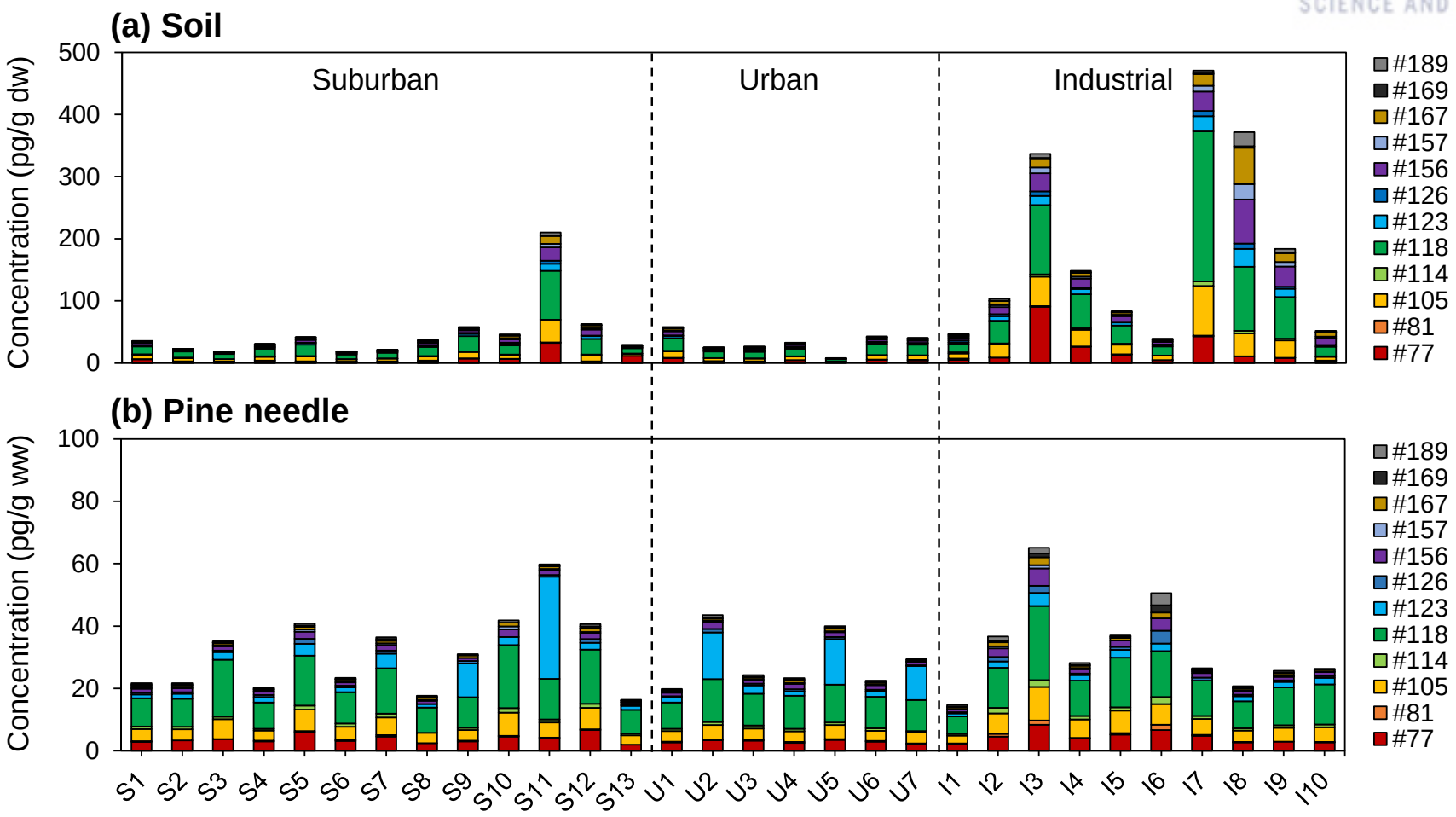

Figure 16. Levels of $\sum_{12}$PCBs in two media in Ulsan, Korea.

3.2.3 Average and individual profiles of dl-PCBs

The average and individual profiles of the dl-PCB congeners for three types of areas and each sampling site are illustrated in Figure 17 and 18, respectively. In Figure 17a, pentachlorobiphenyls (penta-CBs: 105, 114, 118, 123, 126) and hexachlorobiphenyls (hexa-CBs: 156, 157, 167, 169) contributed 85% of the normalized concentrations in soils, and the rest of the dl-PCBs (tetra-CBs: 77, 81 and hepta-CBs: 189) accounted only for 15%. Among the dl-PCB congeners, the concentrations of dl-PCB in soils followed the order of PCB 118 (38%) > PCB 105 (17%) > PCB 77 (13%), and this trend was found at the agricultural soil near e-waste recycling sites in China (Shen et al., 2009).

In Figure 17b, the distribution patterns of dl-PCB congener groups in pine needles were as same as those of soils. PCB 118 was one of the predominant congeners for both soil and pine needle samples, and this congener was reported as a marker of the PCB emission from different industrial thermal processes (Liu et al., 2013; Pham et al., 2019). Since some sampling sites (S9, S11, U2, U5, U7) had the higher compositions of PCB 123 appeared in Figure 18b, the mean fractions of PCB 123 in urban and suburban areas were a little higher than that in the industrial areas, while previous studies had the relatively low contribution of PCB 123 in pine needles (Holt et al., 2016; Tian et al., 2008). It may be assumed that the usage of PCB-related products would cause the deposition of specific congeners to the environmental medium.

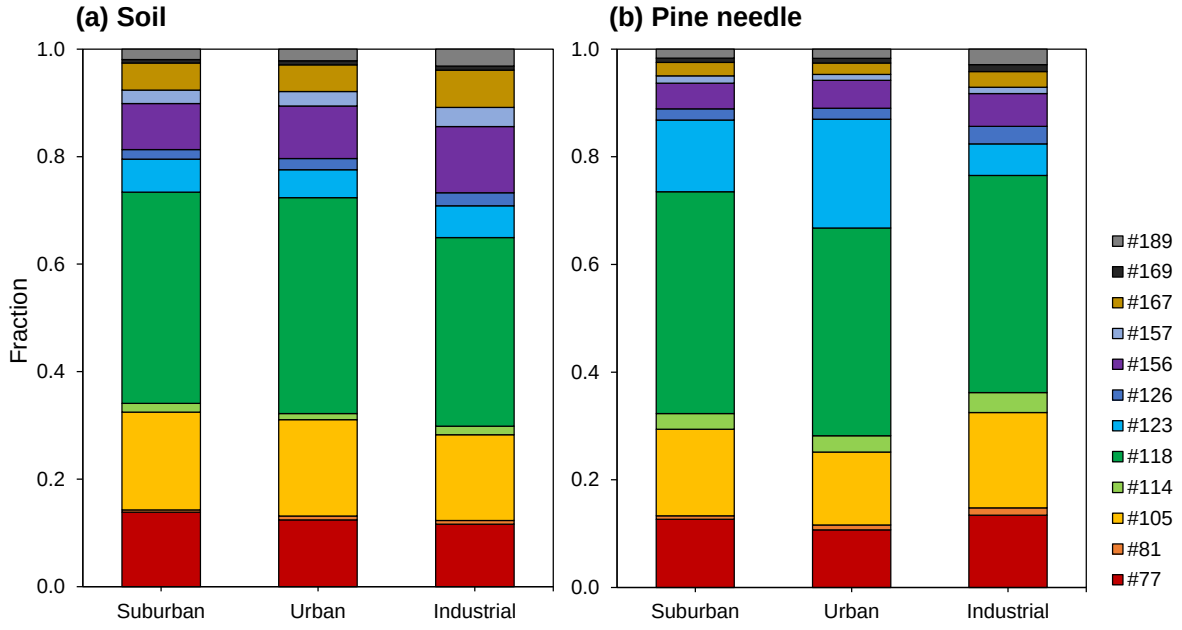

Figure 17. Average congener profiles of dl-PCBs in two media in Ulsan, Korea.

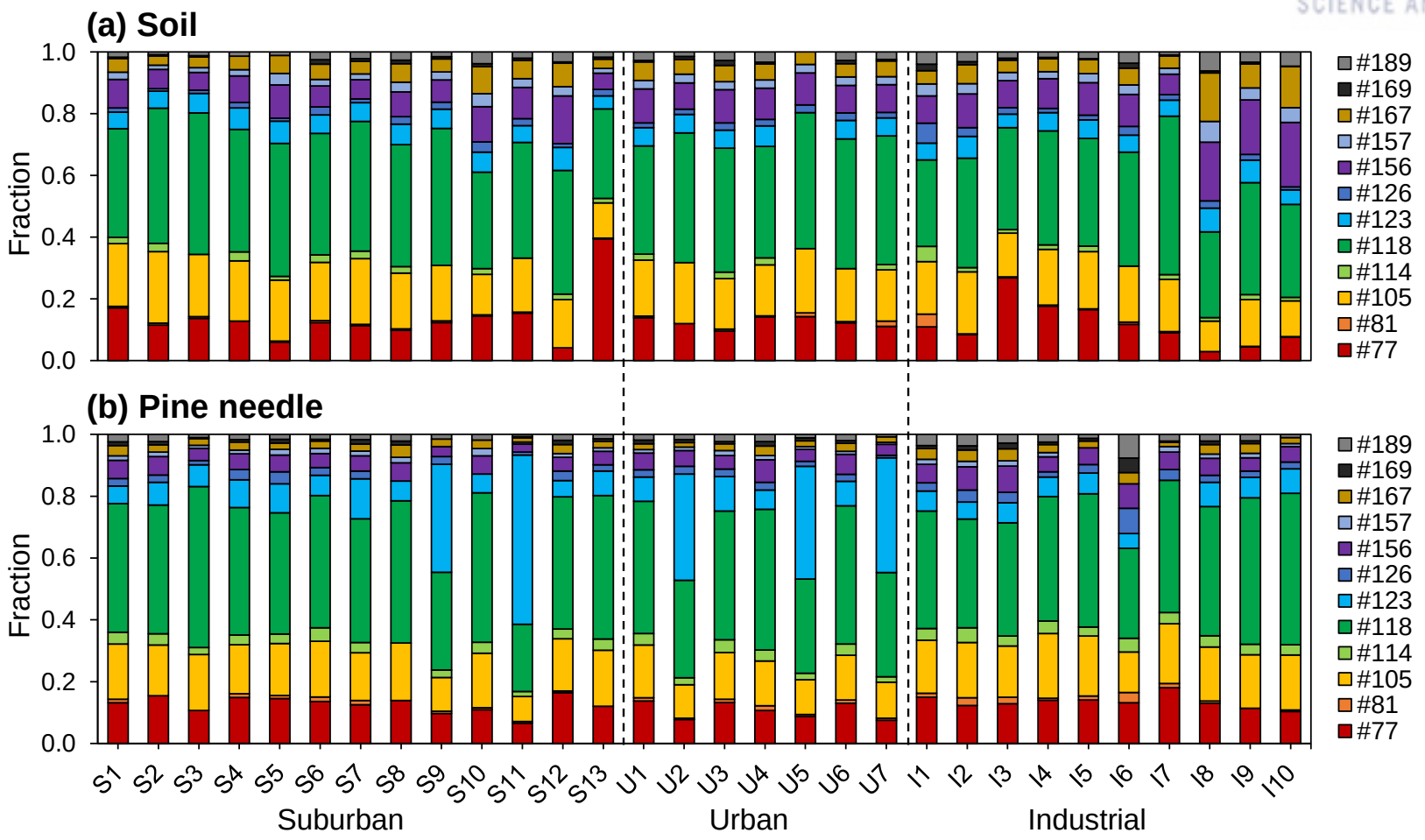

Figure 18. Individual congener profiles of dl-PCBs in two media in Ulsan, Korea.

3.2.4 Principal component analysis of dl-PCBs

The PCA score and loading plots for dl-PCBs in soils from the sampling sites are shown in Figure 19. In the score and the loading plot, the PC 1 and PC 2 accounted for 40% and 24% of the total variance, respectively. The rural samples were located between the rural and suburban samples, indicating a gradual change in dl-PCB profiles from the source (industrial area) to the receptors (urban and suburban areas) might occur (Choi et al., 2012; Nguyen et al., 2016). In the score plot, suburban samples except S10 and S12 were clustered with most urban samples on the left side of the score plot, characterized by high fractions of PCB 105, PCB 77, and PCB 118 in the loading plot. Some samples from industrial areas were too far from the other samples (see the axes for each site in Figure 19). Two industrial sites I8 and I10 were separated from other samples in the score plot with high loadings of PCB 156 and PCB 167, reflecting that they were mainly polluted from the automobile and shipbuilding industries. Moreover, I9 and S12 were on the right side of the score plot, assuming that the suburban site might be polluted from the emission of shipbuilding industries as well. I1, located on the very top side of the score plot (X: 0.22, Y: 4.60), was characterized by slightly higher fractions of PCB 81, PCB 114, PCB 126, and PCB 169 among the sampling sites.

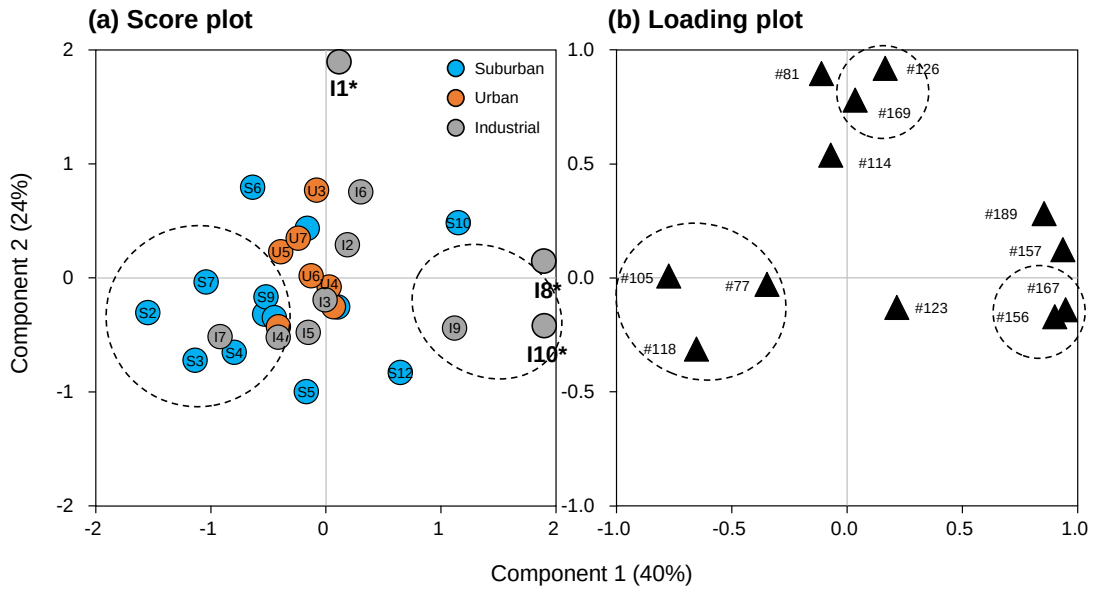

Figure 19. Principal component analysis results of dl-PCBs in soils (**I1**, X: 0.22, Y: 4.6; **I8**, X: 3.35, Y: -0.33; **I10**, X: 2.56, Y: -0.88).

The PCA score and loading plots for dl-PCBs in pine needles from the sampling sites are shown in Figure 20. The PC 1 and PC 2 for the sampling sites accounted for 44% and 28% of the total variance, respectively, Pine needle samples collected near the non-ferrous and petrochemical industries (I1−I7) and those from shipbuilding industries (I9 and I10) were separated from each other in the score plot, suggesting that two samples were characterized by PCB 118 and PCB 157, located on the left side of the loading plot. I6, with higher fractions of PCB 126 compared to other industrial samples, was supported that incomplete combustion during the industrial processes would be the main source of this site (Alcock et al., 1998; Lopez Garcia et al., 1996). Some urban samples (U2, U5, U7) and suburban samples (S8, S9, S11) on the left bottom side of the score plot had relatively high loading of PCB 123, suggesting that local thermal processes (solid residue burning, wood burning) would be the main causes of forming such congener (Pereira, 2004).

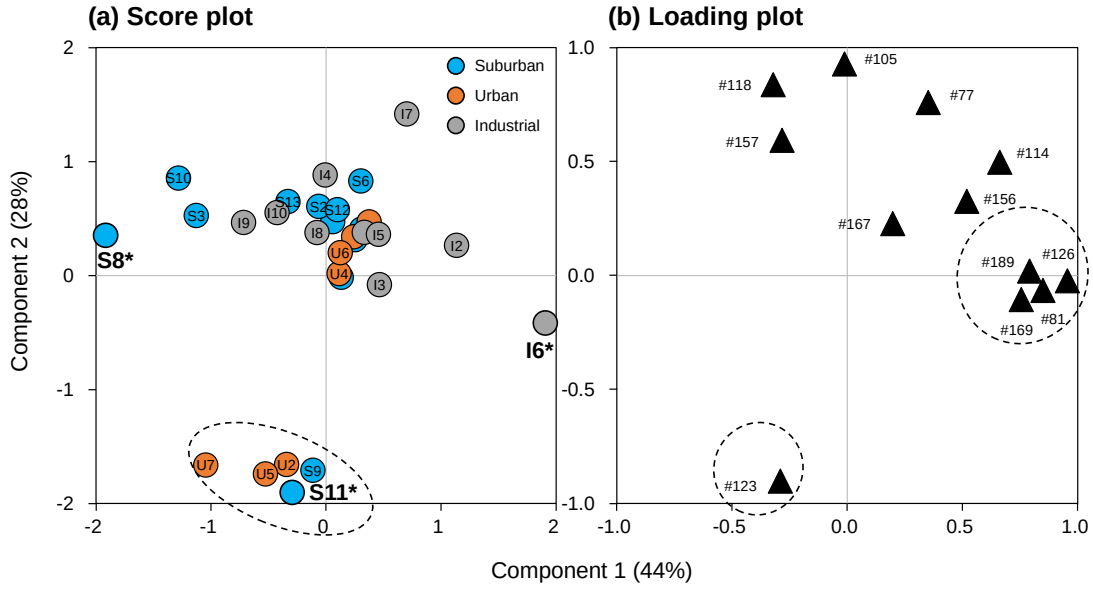

Figure 20. Principal component analysis results of dl-PCBs in pine needles (**I6**, X: 3.93, Y: -1.34; **S11**, X: -0.80, Y: -2.87; **S8**, X: -2.20, Y: 0.12).

3.3 Distribution of indicator PCBs in soils and pine needles

3.3.1 Total concentrations of indicator PCBs

A summary of the indicator PCB concentrations in soils and pine needles for all sites is shown in Figure 21. In Figure 21a, the concentrations of $\sum_7$PCBs in soils ranged between 59.29−3,548.55 pg/g dw (mean: 452.98 pg/g dw), and the indicator levels from the industrial sites were not significantly correlated with those from suburban (Mann-Whitney rank sum test, $p < 0.01$) and urban sites (Mann-Whitney rank sum test, $p < 0.05$). This result supports the previous studies (Liu et al., 2020; Nguyen et al., 2016) which suggested that relatively high PCB concentrations in soils near the industrial complex have occurred.

The total seven indicator PCB concentrations ranged between 68.14−311.42 pg/g ww (mean: 166.37 pg/g ww) in pine needles (Figure 21b). Mean concentrations of indicator PCBs from industrial sites (179.76 pg/g ww) were similar to those from suburban and urban sites (161.36 pg/g ww), giving no significant difference ($p > 0.05$). The results showed that the trend of total indicator PCB concentration for each site is hard to represent the regional characterization owing to the uses of commercial products (usually Aroclors) and electrical equipment (dielectric fluid, stationary transformers, capacitors, etc.) regardless of the locations (UMTA, 1984).

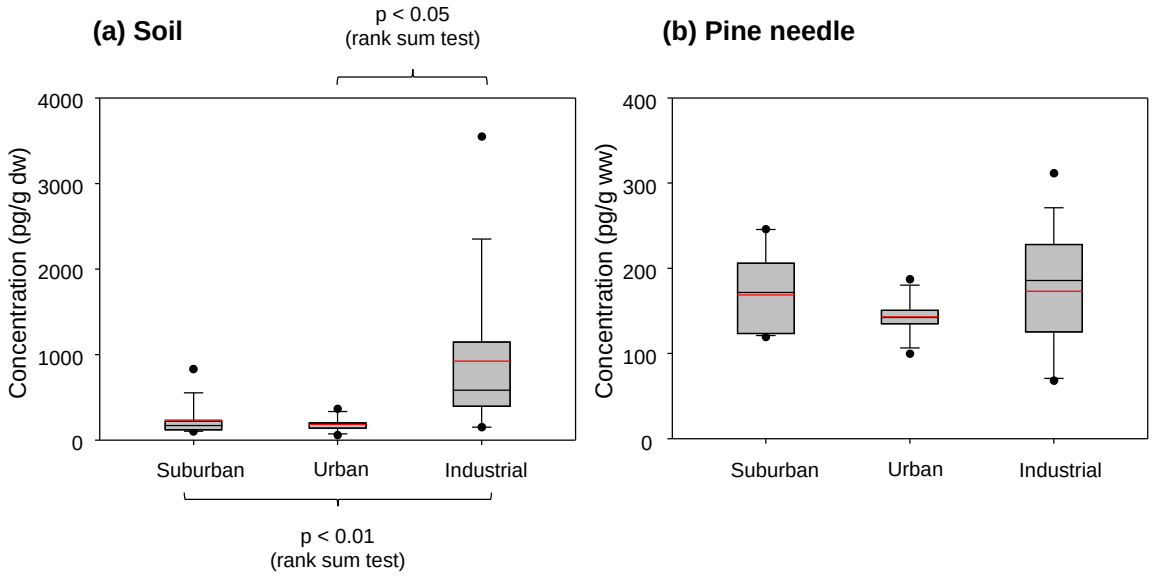

Figure 21. Box plots $\sum_7$PCBs in two media in Ulsan, Korea.

3.3.2 Spatial distribution of indicator PCBs

The spatial distributions of total seven indicator PCB levels in soil and pine needle samples are displayed in Figure 22. In general, industrial areas were shown the higher concentrations of indicator PCBs in soils than those from suburban and urban areas. The industrial site I8 was having the highest concentration owing to the area where automobile industries are located, whereas sites such as indicator PCB levels in I2 and I3 were relatively low due to the areas near the non-ferrous industries.

The stacked bar graphs of indicator PCB congeners in concentrations at all sites are shown in Figure 23. In Figure 23a, most industrial sites showed higher concentrations of indicator PCBs in soils than those in other areas, and this result is consistent with those from the previous study taken in the same place, Ulsan, and I8 had the highest concentration of indicator PCBs among the sampling sites owing to the influence on automobile activities (Nguyen et al., 2016).

In Figure 23b, the patterns of indicator PCBs in pine needles among the sampling sites have not appeared. In comparisons with sampling sites, some industrial sites such as I1 and I7 had relatively low indicator PCB levels in pine needles. Those sites may be less polluted due to the locations where the canopy effect had happened (Simonich et al., 1995).

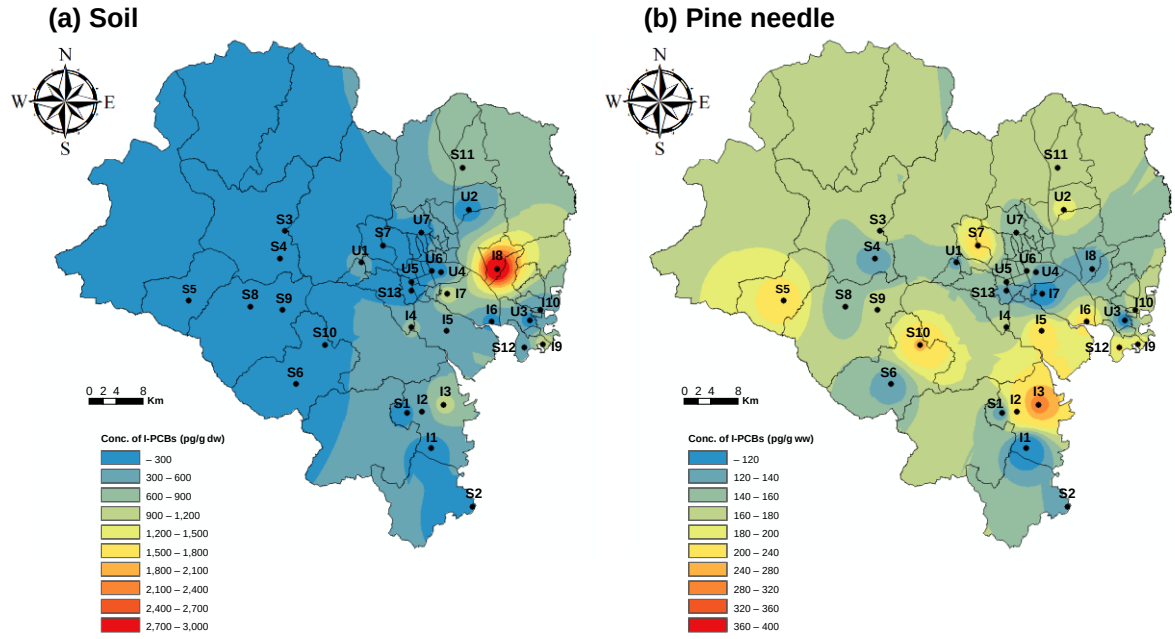

Figure 22. Contour maps of $\sum_7$PCBs in two media in Ulsan, Korea.

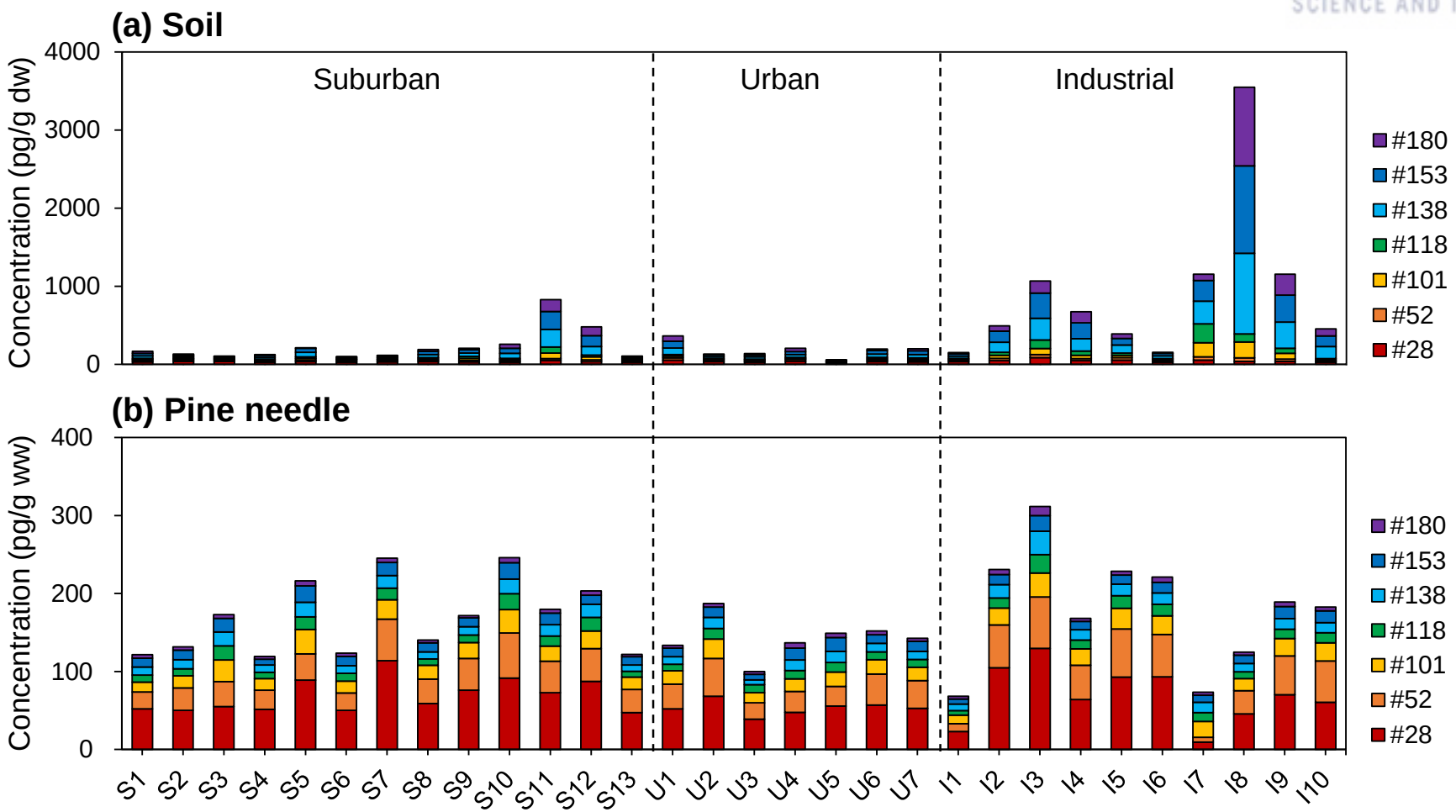

Figure 23. Levels of $\sum_7$PCBs in two media in Ulsan, Korea.

3.3.3 Average and individual profiles of indicator PCBs

The average and individual profiles of the indicator PCB congeners for three areas and each sampling site are illustrated in Figure 24 and 25, respectively. In Figure 24a, soil samples generally had the higher contents of two higher chlorinated PCB congener groups, PCB 138, PCB 153 (hexa-CBs), accounting for 44% of the normalized concentrations. Based on these results, it can be referred that dry and wet deposition between soil and PCBs was well performed due to the physicochemical properties of soil. The lower chlorinated PCB congener groups, especially tri-CBs (PCB 28) and tetra-CBs (PCB 52), were volatilized back into the atmosphere, leading to the lowest ratio compared to other PCB congener groups.

In Figure 24b, pine needle, on the contrary, had a high proportion of tri-CBs (38% of $\sum_7$PCBs), which leads to the different distribution pattern of indicator PCBs in soil (17% of $\sum_7$PCBs). This result implies that lower chlorinated PCBs are more likely absorbed into the pine needles, but higher chlorinated PCBs are normally washed off from the needles due to the dry deposition in the particulate phase (Chun, 2009).

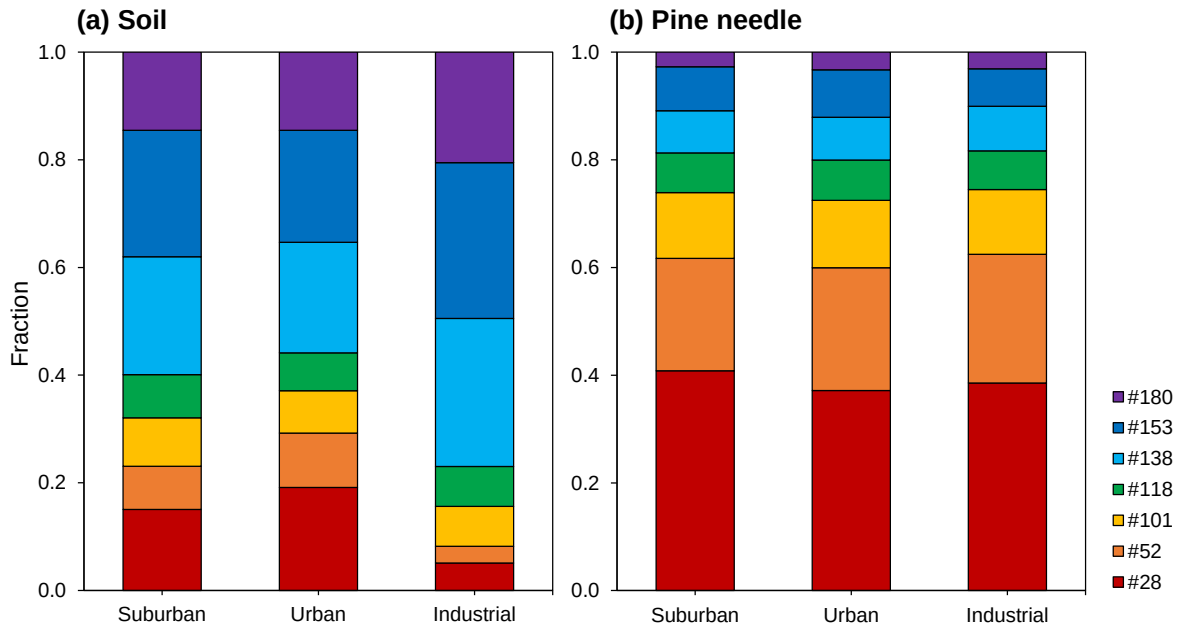

Figure 24. Average congener profiles of indicator PCBs in two media in Ulsan, Korea.

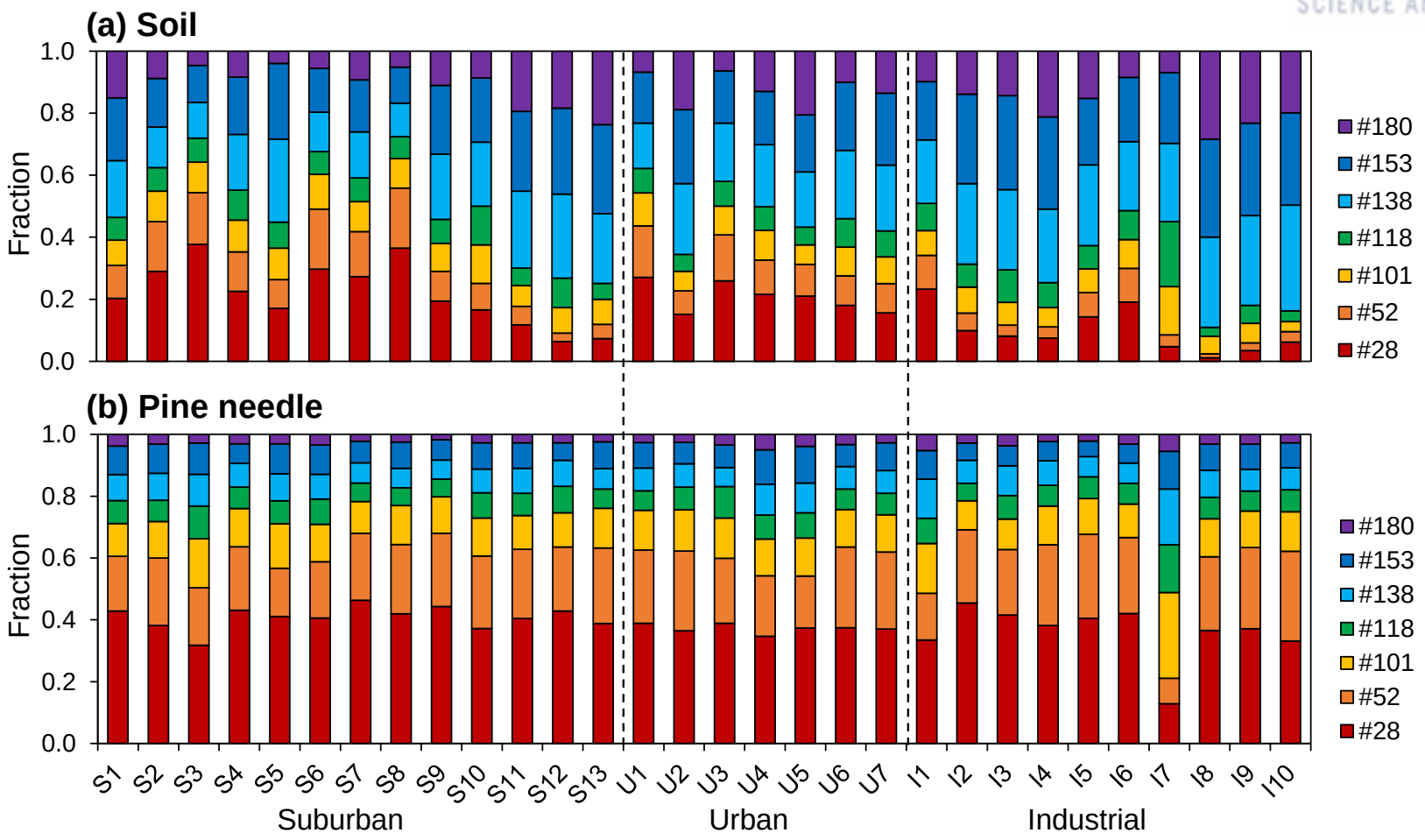

Figure 25. Individual congener profiles of indicator PCBs in two media in Ulsan, Korea.

3.3.4 Principal component analysis of indicator PCBs

The PCA score and loading plots for indicator PCBs in soils and pine needles from the sampling sites are shown in Figure 26 and Figure 27, including the commercial products called Aroclor 1254 and 1260 as input data for PCA to compare the contamination profiles of each medium and to identify the potential PCB emission sources on the basis of PCA results (Frame et al., 1996; Nguyen et al., 2016).

The PCA score and loading plots for indicator PCBs in soils from the sampling sites are shown in Figure 26, and the PC 1 and PC 2 accounted for 64% and 26% of the total variance. I7, located on the top right side of the score plot, was characterized by high loadings of PCB 101 and PCB 118 in the loading plot, and Aroclor 1254 was located in the same position, which was out of range in the score plot (X: 0.20, Y: 4.17). It was suggested that soil samples from this site were mainly affected by the usage or leakage of transformer oil from petrochemical plants. Since the transformer oil had used for transferring electrical power as an energy supply especially in petrochemical industries, Aroclor 1254 was the main component of transformer oil (Hong et al., 2005; Nguyen et al., 2016). Moreover, soil samples from automobile (I8) and shipbuilding industrial complexes (I9 and I10) were clustered into the same group as Aroclor 1260, with similar congener profiles of higher chlorinated PCBs including PCB 138, PCB 153, and PCB 180. This reflects that anti-fouling paints containing PCBs had been used for ships as extenders for preventing microbial spoilage, and a massive amount of higher chlorinated PCBs had been deposited into the soil due to the spillage of PCB-containing product (Edge et al., 2001; Nguyen et al., 2016).

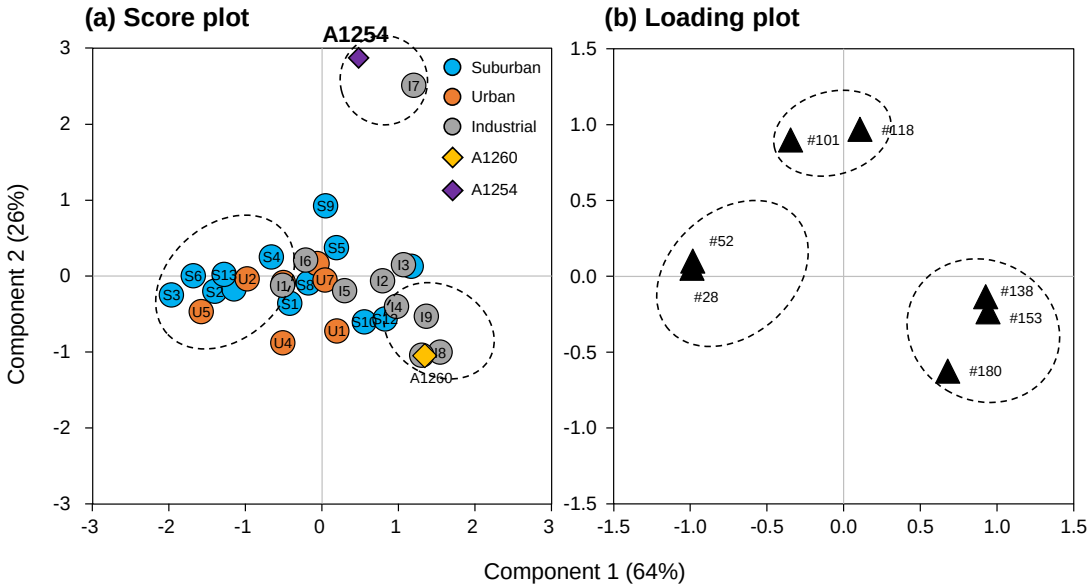

Figure 26. Principal component analysis results of indicator PCBs in soils (**Aroclor 1254**, X: 0.20, Y: 4.17).

The PCA score and loading plots for indicator PCBs in pine needles from the sampling sites are shown in Figure 27, and the PC 1 and PC 2 accounted for 62% and 31% of the total variance. The pine needle sample from I7, as mentioned earlier, had a similar tendency of indicator PCBs in soil. The commercial product called Aroclor 1254 was in the same position as I7, which was out of range in the score plot (X: 1.16, Y: 2.96). It can be referred that the main source of soil and pine needle samples in this site was derived from the petrochemical industrial complex, in which the usage of Aroclor 1254 as transformer oil was suspected. Unlike soil, pine needle samples collected from I9 and I10 were positioned on the bottom left side of the score plot, whereas Aroclor 1260 was on the opposite side. It was expected the deposition of organic pollutants in the soil for a long period would be possible to identify the historical uses of commercial products that had been banned since the mid-90s. In that case, this result implied that the application in the commercial product for shipbuilding and automobile industries had stopped for recent years.

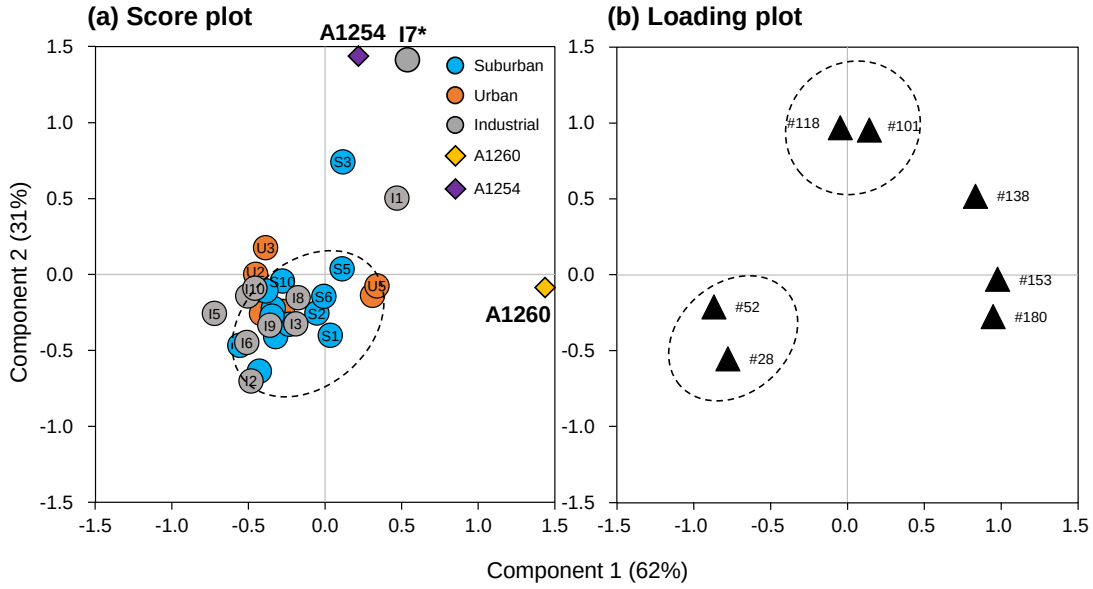

Figure 27. Principal component analysis results of indicator PCBs in pine needles (**I7**, X: 1.16, Y: 2.96; **Aroclor 1254**, X: 0.65, Y: 4.00; **Aroclor 1260**, X: 5.03, Y: -1.69).

3.4 Global comparisons of target compounds

3.4.1 Comparisons of PCDD/F concentrations

The measured levels of PCDD/Fs in soils and pine needles between this study and previous studies are listed in Table 6. The mean PCDD/F levels at suburban, urban, and industrial areas in this study were 47.82, 47.19, 138 pg/g dw for soils, and 4.27, 4.14, 10.33 pg/g ww for pine needles, respectively (only the ranges and mean values of total PCDD/F concentrations are shown in this table).

When comparing the results from the previous studies, the mean PCDD/F levels of soils in industrial areas in this study were higher than 60.14 pg/g dw from Spain (Schuhmacher et al., 2004) and 1.22 pg/g dw from industrial waste incinerator (IWI) in Korea (Kim et al., 2005), but lower than 14.3−258.9 pg/g dw from electronic waste recycling area (Tang et al., 2014) and 1,320 pg/g dw from industrial areas near Pearl River Delta (Zhang et al., 2009) in China. The results from this study in suburban and urban sites were relatively lower than 17.54, 259.17 pg/g dw from Spain (Schuhmacher et al., 2004) and 2,504, 2,335 pg/g dw from the sites near Pearl River Delta (Zhang et al., 2009), respectively. By comparing the TEQ concentrations with this study, the total TEQ concentration at sampling sites in this study was much lower than those in other locations, except 0.45 pg-TEQ/g dw from entire sites in Spain (Schuhmacher et al., 2004) and 1.22 pg-TEQ/g dw from IWI in Korea (Kim et al., 2005).

When comparing the results of pine needles from those from the previous studies, both mean PCDD/F levels and total PCDD/F concentration ranges at all sampling areas in this study were quite lower than those in previous studies, except 13.5−17.4 pg/g dw from Czech, Germany (Kirchner et al., 2006). In the comparison of the TEQ concentrations in this study, the total TEQ concentrations in the previous studies except 0.11−0.19 pg-TEQ/g dw from Czech (Kirchner et al., 2006) and 0.01−1.28 pg-TEQ/g ww from four sites in Poland (Bochentin et al., 2007) were higher.

Table 6. Global comparisons of PCDD/F concentrations in soils and pine needles between this study and other studies (mean values are marked in bold).

Sampling area	Sample type	Compounds	Concentration	TEQ	Unit	Reference
Industrial (Spain)	soils	17 PCDD/Fs	**60.14**	**0.45** [a]	pg/g dw	Schuhmacher et al., 2004
Urban (Spain)	soils	17 PCDD/Fs	**259.17**	**1.26** [a]	pg/g dw	
Rural (Spain)	soils	17 PCDD/Fs	**17.54**	**0.16** [a]	pg/g dw	
IWI (Korea)	soils	17 PCDD/Fs	0−23.88	1.22[c]	pg/g dw	Kim et al., 2005
Deserted land (China)	soils	17 PCDD/Fs	**688**	**7.18**[b]	pg/g dw	Liu et al., 2009
E-waste recycling (China)	soils	17 PCDD/Fs	218−3,122	14.3−258.9[c]	pg/g dw	Tang et al., 2014
Suburban (PRD)	soils	17 PCDD/Fs	2,504	3.99[a]	pg/g dw	Zhang et al., 2009
Industrial (PRD)	soils	17 PCDD/Fs	1,320	4.8[a]	pg/g dw	
Residential (PRD)	soils	17 PCDD/Fs	2,335	2.63[a]	pg/g dw	
Ulsan, Korea	soils	17 PCDD/Fs	8.83−237.96 (**77.73**)	0.03−6.06 (**1.195**)[b]	pg/g dw	This study
5 cities (Korea)	pine needles	17 PCDD/Fs	28.32−554.33	2.19−26.88[c]	pg/g dw	Ok et al., 2002
Tokyo bay (Japan)	pine needles	17 PCDD/Fs	27−110	2.69−11.07[b]	pg/g ww	Hanari et al., 2004
Dalian (China)	pine needles	17 PCDD/Fs	**127**	**2.1**[a]	pg/g dw	Chen et al., 2006
Czech (Germany)	pine needles	17 PCDD/Fs	**13.5−17.4**	**0.11−0.19**[c]	pg/g dw	Kirchner et al., 2006
4 cites (Poland)	pine needles	17 PCDD/Fs	3.5−125	0.01−1.28[c]	pg/g ww	Bochentin et al., 2007
38 cities (China)	pine needles	17 PCDD/Fs	5.39−330.1	0.07−17.37[b]	pg/g dw	Chen et al., 2012
China(garden)	pine needles	17 PCDD/Fs	3.92−95.19	0.35−7.54[b]	pg/g dw	Mei et al., 2016
Campus	pine needles	17 PCDD/Fs	6.53−69.46	1.88−8.39[b]	pg/g dw	
MWIP	pine needles	17 PCDD/Fs	59.96−115.91	17.59−28.47[b]	pg/g dw	
Ulsan, Korea	pine needles	17 PCDD/Fs	1.22−36.4, (**6.26**)	0.06−2.53 (**0.372**)[b]	pg/g ww	This study

a - WHO_{1998}, b - WHO_{2005}, c - $I\text{-}TEF_{1988}$ (NATO); ww: wet weight, dw: dry weight; PRD: Pearl River Delta, China

3.4.2 Comparisons of PCB concentrations

The measured levels of 18 PCBs in soils and pine needles between this study and previous studies are listed in Table 7. The mean concentrations of dl-PCBs at suburban, urban, and industrial areas in this study were 48.65, 32.19, 183.74 pg/g dw for soils, and 31.29, 28.97, 33.13 pg/g ww for pine needles, respectively. Moreover, the average values of indicator PCBs at suburban, urban, and industrial areas in this study were 234, 186.12, 924.46 pg/g dw for soils, and 168.69, 142.95, 179.76 pg/g ww for pine needles (only the ranges and mean values of total PCB concentrations were shown in the table).

When comparing the 18 PCB results from the previous studies, the mean PCB levels of soils at sampling areas in this study were higher than 2.09−62.85 pg/g dw from Turkey (Hanedar et al., 2019) and N.D.−1908 pg/g dw from Pakistan (Ullah et al., 2020), but lower than 350−50,800 pg/g dw from electronic waste recycling area in China (Liu et al., 2020). In the comparison of the TEQ concentrations in this study, they were much lower than those in other studies, except 0.29 and 0.007 pg-TEQ/g dw from e-waste dismantling and recycling sites in China (Liu et al., 2020). Even though electronic waste disposal was the main source of dl-PCBs, relatively low TEQ concentrations in Liu's study were shown in this table.

When comparing the results of pine needles from those from the previous studies, both mean PCB levels and total PCB concentration ranges at all sampling areas in this study was lower than those in previous studies, except 110−420 pg/g ww from the sites near the Tokyo bay, Japan (Hanari et al., 2004). In the case of TEQ concentrations of pine needles, all other sites except sites near Tokyo bay (Hanari et al., 2004) and sites from Europe (Holt et al., 2016) showed moderate and lower total TEQ concentrations compared to the results of this study.

Table 7. Global comparisons of PCB concentrations in soils and pine needles between this study and other studies (mean values are marked in bold).

Sampling area	Sample type	Compounds	Concentration	TEQ	Unit	Reference
Deserted land (China)	soils	12 PCBs	**6,010**	0.02−5.04[b*]	pg/g dw	Liu et al., 2009
China	soils	36 PCBs	11−100,000	0.42−11[b]	pg/g dw	Shen et al., 2009
Turkey	soils	15 PCBs	2.09−62.85	-	pg/g dw	Hanedar et al., 2019
E-waste dismantling (China)	soils	19 PCBs	11,700−26,100	0.29[b]	pg/g dw	Liu et al., 2020
E-waste recycling (China)	soils	19 PCBs	350−50,800	0.007[b]	pg/g dw	
4 river (Pakistan)	soils	33 PCBs	N.D. to 1,908	0.539[b]	pg/g dw	Ullah et al. 2020
Ulsan, Korea	soils	18 PCBs	64−15,269 (**208.98**)	0.02−0.96 (**31.36**)[b]	pg/g dw	This study
Tokyo bay (Japan)	pine needles	12 PCBs	110−420	0.56−1.30[b]	pg/g ww	Hanari et al., 2004
Dalian (China)	pine needles	209 PCBs	**4,389**	0.4[a]	pg/g dw	Chen et al., 2006
Semi- and urban (Croatia)	pine needles	17 PCBs	1,620−27,140	<0.5[a]	pg/g dw	Romanić et al., 2006
U.S. Superfund	pine needles	29 PCBs	15,000−34,000	0.24−0.48[a]	pg/g dw	Loganathan et al., 2008
U.S. Residential	pine needles	29 PCBs	5,200−12,000	0.03−0.06[a]	pg/g dw	
U.S. Industrial	pine needles	29 PCBs	1,900−8,400	0.03−0.11[a]	pg/g dw	
Europe	pine needles	18 PCBs	220−5,100	0.05−1.7[b]	pg/g dw	Holt et al., 2016
Ulsan, Korea	pine needles	18 PCBs	77−353 (**185.54**)	<0.49 (**166.37**)[b]	pg/g ww	This study

[a]WHO_{1998}, [b]WHO_{2005}, [c]I-TEF (NATO); ww: wet weight, dw: dry weight; N.D.: not detected; *TEQ of ∑PCDD/Fs and ∑PCBs
12 PCB congeners: dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)
15 PCB congeners: 18, 20, 28, 31, 52, 44, 101, 105, 118, 138, 149, 153, 170, 180, 194
17 PCB congeners: 6 indicator PCBs (28, 52, 101, 138, 153,180), 9 dioxin-like PCBs (74, 105, 114, 118, 123, 156, 157, 167, 189) and other congeners (60, 170)
18 PCB congeners: 6 indicator PCBs (28, 52, 101, 138, 153,180) and 12 dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)
19 PCB congeners: 12 dioxin-like PCBs, 6 indicator PCBs and PCB-189/209
29 PCB congeners: 8, 48, 29, 28/50, 52, 104, 44, 101, 87, 154, 118, 153, 105, 138, 187, 202, 201, 180, 200, 170, 198, 199, 196, 208, 195, 207, 194, 206, 209
33 PCB congeners: 8 dioxin-like PCBs (77, 126, 169, 105, 114, 118, 156, 189) and non-dioxin-like PCBs (8, 28, 30, 37, 44, 49, 52, 60, 66, 70, 74, 82, 87, 99, 101, 128, 138, 153, 158, 166, 170, 179, 180, 183, 198)
36 PCB congeners: 12 dioxin-like PCBs, 6 indicator PCBs, and 17 non-dioxin-like PCBs

3.5 Spearman correlation results

3.5.1 Correlations between PCDD/Fs, TOC, and lipid content

The correlations between PCDD/Fs, $\sum_{17}$PCDD/Fs, $\sum_{7}$PCDDs, $\sum_{10}$PCDFs, and TOC content in soils were determined by Spearman correlation analysis (Table 8). PCDD/F congeners were correlated with each other and even total 17 PCDD/Fs, sum of PCDDs and PCDFs, except some congeners (2,3,7,8-TCDD, 1,2,3,4,7,8-HxCDD, and OCDD). Among the PCDD/F congeners, 2,3,7,8-TCDDs not only had no correlations between some congeners but also had no relation between $\sum_{7}$PCDDs owing to the relatively low contribution in soil.

TOC had no significant correlations with $\sum_{17}$PCDD/Fs, $\sum_{7}$PCDDs except $\sum_{10}$PCDFs ($r = 0.452$, $p < 0.05$) and all PCDD congeners except 1,2,3,4,6,7,8-HpCDD and some PCDF congeners (1,2,3,7,8-PCDF and 1,2,3,7,8,9-HxCDF). It is suggested that most polychlorinated furans (PCDFs) have a strong tendency of binding to organic carbons while polychlorinated dioxins (PCDDs) are directly accumulated on the soil surface through domestic burning and industrial processes (Cho et al., 2019; Moon et al., 2012).

The correlations between PCDD/Fs, $\sum_{17}$PCDD/Fs, $\sum_{7}$PCDDs, $\sum_{10}$PCDFs, and lipid content in pine needles were examined by Spearman correlation analysis in the exclusion of three congeners (2,3,7,8-TCDD, 1,2,3,7,8-PCDD, and 1,2,3,7,8,9-HxCDD) under the 50% of detection rates (Table 9). Unlike the correlation results in soils, PCDD/Fs in pine needles were correlated with each other except OCDD, total 17 PCDD/Fs except OCDF, and the sum of PCDDs and PCDFs except some congeners. This finding can be implied that the photodegradation rates of PCDD/Fs on pine needles may be faster than on particulate matter in the air due to the formation of free electrons and reactive radicals from sunlight absorption, and therefore, higher chlorinated compounds (OCDD, OCDF) would possibly be photolyzed (Niu et al., 2003).

Many studies had already reported that higher lipid content in pine needles would have higher levels of contaminants such as POPs, PAHs, and so on (Chun, 2013; Mei et al., 2016; Romanić et al., 2006). However, lipid content was not correlated with PCDD/Fs according to the correlation result, assuming that lipid content is not the only factor that matters with the concentration level in organic substances. Other characteristics of pine needles such as longevity, wax content, surface area, and external factors (temperature and wind flow) would affect the accumulation of pollutants mentioned in the previous studies (Chen, 2016; Odabasi et al., 2015; Tomashuk et al., 2012).

Table 8. Spearman correlations between PCDD/Fs, $\sum_{17}$PCDD/Fs, $\sum_{7}$PCDDs, $\sum_{10}$PCDFs and TOC (%) in soils.

	2378-TCDD	12378-PCDD	123478-HxCDD	123678-HxCDD	123789-HxCDD	1234678-HpCDD	OCDD	2378-TCDF	12378-PCDF	23478-PCDF	123478-HxCDF	123678-HxCDF	234678-HxCDF	123789-HxCDF	1234678-HpCDF	1234789-HpCDF	OCDF	∑PCDD/Fs	∑PCDDs	∑PCFDs	TOC
2378-TCDD	1	**.457***	**.407***	**.385***	**.377***	**.400***	.253	.360	.339	**.418***	.355	**.418***	**.400***	**.374***	**.384***	.359	**.370***	**.387***	.342	**.370***	-.187
12378-PCDD		1	**.502****	**.748****	**.620****	**.726****	**.431***	**.777****	**.764****	**.745****	**.747****	**.743****	**.764****	**.777****	**.732****	**.669****	**.694****	**.630****	**.527****	**.759****	.251
123478-HxCDD			1	**.515****	.301	**.551****	**.361***	**.447***	**.516****	**.515****	**.439***	**.520****	**.465****	.323	**.483****	**.473****	**.424***	**.479****	**.436***	**.481****	.038
123678-HxCDD				1	**.779****	**.875****	**.526****	**.755****	**.881****	**.889****	**.884****	**.907****	**.891****	**.561****	**.884****	**.809****	**.792****	**.729****	**.610****	**.850****	.353
123789-HxCDD					1	**.699****	**.424***	**.514****	**.640****	**.692****	**.675****	**.703****	**.698****	**.565****	**.674****	**.556****	**.549****	**.599****	**.506****	**.605****	.065
1234678-HpCDD						1	**.692****	**.676****	**.802****	**.872****	**.893****	**.902****	**.867****	**.619****	**.960****	**.819****	**.924****	**.882****	**.793****	**.952****	**.417***
OCDD							1	.300	**.465****	**.416***	**.505****	**.461***	**.394***	.326	**.556****	**.461***	**.604****	**.918****	**.979****	**.588****	.126
2378-TCDF								1	**.833****	**.788****	**.758****	**.772****	**.743****	**.656****	**.700****	**.676****	**.709****	**.524****	**.388***	**.751****	**.388***
12378-PCDF									1	**.922****	**.919****	**.886****	**.862****	**.663****	**.857****	**.833****	**.823****	**.697****	**.560****	**.870****	.355
23478-PCDF										1	**.918****	**.931****	**.946****	**.715****	**.914****	**.879****	**.826****	**.667****	**.531****	**.897****	**.375***
123478-HxCDF											1	**.926****	**.918****	**.655****	**.958****	**.823****	**.926****	**.754****	**.618****	**.951****	**.377***
123678-HxCDF												1	**.930****	**.620****	**.930****	**.851****	**.859****	**.692****	**.570****	**.909****	**.467****
234678-HxCDF													1	**.693****	**.927****	**.882****	**.812****	**.635****	**.499****	**.893****	**.438***
123789-HxCDF														1	**.629****	**.589****	**.586****	**.519****	**.410***	**.658****	.174
1234678-HpCDF															1	**.854****	**.952****	**.794****	**.671****	**.982****	**.422***
1234789-HpCDF																1	**.799****	**.667****	**.549****	**.854****	**.453***
OCDF																	1	**.831****	**.716****	**.976****	**.435***
∑PCDD/Fs																		1	**.967****	**.820****	.191
∑PCDD																			1	**.699****	.152
∑PCDF																				1	**.452***

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 9. Spearman correlations between PCDD/Fs, $\sum_{17}$PCDD/Fs, $\sum_{7}$PCDDs, $\sum_{10}$PCDFs and lipid content (%) in pine needles.

	123478-HxCDD	123678-HxCDD	1234678-HpCDD	OCDD	2378-TCDF	12378-PCDF	23478-PCDF	123478-HxCDF	123678-HxCDF	234678-HxCDF	123789-HxCDF	1234678-HpCDF	1234789-HpCDF	OCDF	∑PCDD/Fs	∑PCDDs	∑PCDFs	Lipid
123478-HxCDD	1	**0.999****	**.468****	.354	**.432***	**.433***	**.451***	**.433***	**.444***	**.488****	**.500****	**.433***	**0.999****	**.461***	**.433***	**.433***	**.433***	-.079
123678-HxCDD		1	**.468****	.354	**.432***	**.433***	**.451***	**.433***	**.444***	**.488****	**.500****	**.433***	**0.999****	**.461***	**.433***	**.433***	**.433***	-.079
1234678-HpCDD			1	.320	.258	.216	.311	**.364***	**.498****	**.616****	.339	**.577****	**.468****	**.703****	**.527****	**.604****	**.492****	-.066
OCDD				1	.341	.297	.288	.216	.210	.216	.219	.234	.354	.234	**.575****	**.916****	.319	-.013
2378-TCDF					1	**.673****	**.612****	**.671****	**.380***	**.394***	.074	**.546****	**.432***	-.025	**.695****	**.462***	**.684****	-.251
12378-PCDF						1	**.667****	**.664****	**.554****	**.419***	.209	**.577****	**.433***	.176	**.821****	**.376***	**.836****	-.170
23478-PCDF							1	**.373***	.321	.179	.109	**.401***	**.451***	.129	**.658****	**.392***	**.590****	.020
123478-HxCDF								1	**.525****	**.529****	.254	**.805****	**.433***	.236	**.691****	.342	**.816****	-.173
123678-HxCDF									1	**.392***	**.382***	**.543****	**.444***	**.618****	**.599****	.340	**.670****	.059
234678-HxCDF										1	**.370***	**.702****	**.488****	**.456***	**.586****	**.437***	**.650****	-.104
123789-HxCDF											1	.283	**.500****	**.429***	.298	.283	.283	-.124
1234678-HpCDF												1	**.433***	**.455***	**.800****	**.456***	**.893****	-.133
1234789-HpCDF													1	**.461***	**.433***	**.433***	**.433***	-.079
OCDF														1	.356	**.400***	**.399***	.258
∑PCDD/Fs															1	**.727****	**.927****	-.168
∑PCDD																1	**.494****	-.036
∑PCDF																	1	-.166

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

3.5.2 Correlations between PCBs, TOC, and lipid content

The correlations between PCBs, $\sum_{18}$PCBs, and TOC in soils were determined by Spearman correlation analysis (Table 10). PCB congeners were correlated with each other and even $\sum_{18}$PCBs, except three congeners (PCB 52, PCB 81, PCB 114). However, the sum of 18 PCBs was correlated with all PCB congeners (r between 0.408 and 0.992), supporting that soil has been primarily polluted from PCBs due to the massive uses of PCB related products and incomplete combustions.

TOC had significantly positive correlations with PCB 126 ($r = 0.491$, $p < 0.01$) and PCB 169 ($r = 0.535$, $p < 0.01$), indicating that higher organic carbon contents may be attributed to the strong binding affinity of these congeners in the soil. Some lower chlorinated PCBs (tri- to tetra-) were having no correlation between TOC, because volatilization depending on the atmospheric temperatures and lower K_{oa} would be the main cause of this correlation result (Li et al., 2006; Yeo et al., 2004).

The correlations between PCBs, $\sum_{18}$PCBs, and lipid content in pine needles were examined by Spearman correlation analysis (Table 11). PCBs in pine needle were correlated with each other and some congeners had no correlation. The sum of 18 PCBs, as well as that in soil, was correlated with PCB compounds, assuming that atmospheric PCBs are ubiquitous in surroundings via long-range transport (Kannan et al., 2009; Simonich et al., 1995).

Based on this result, lipid content was negatively correlated with some congeners (PCB 118, PCB 123, PCB 138) and $\sum_{18}$PCBs. This result supports that PCBs including penta-CBs (PCB 118, PCB 123) and hexa-CBs (PCB 138) prefer to do the particle-bound deposition onto the plant surface in the presence of small lipid content (Liu et al., 2013).

Table 10. Spearman correlations between PCBs, $\sum_{18}$PCBs, and TOC (%) in soils.

	#28	#52	#77	#81	#101	#105	#114	#118	#123	#126	#138	#153	#156	#157	#167	#169	#180	#189	∑PCBs	TOC
#28	1	**.858****	**.588****	**.441***	**.647****	**.714****	**.512****	**.657****	**.677****	**.519****	**.596****	**.612****	**.575****	**.572****	**.535****	**.482****	**.584****	**.535****	**.644****	.295
#52		1	**.578****	.252	**.719****	**.726****	**.556****	**.698****	**.689****	**.507****	**.665****	**.682****	**.632****	**.607****	**.602****	**.472****	**.624****	**.571****	**.691****	.278
#77			1	**.549****	**.723****	**.762****	**.512****	**.755****	**.754****	**.815****	**.711****	**.715****	**.751****	**.755****	**.693****	**.680****	**.700****	**.756****	**.731****	.359
#81				1	**.449***	**.567****	.286	**.517****	**.483****	**.612****	**.396***	**.408***	**.446***	**.467****	**.423***	**.606****	**.377***	**.479****	**.408***	.333
#101					1	**.937****	**.576****	**.982****	**.964****	**.795****	**.955****	**.963****	**.933****	**.905****	**.929****	**.682****	**.867****	**.830****	**.956****	**.406***
#105						1	**.621****	**.969****	**.961****	**.829****	**.892****	**.903****	**.915****	**.901****	**.882****	**.700****	**.800****	**.822****	**.905****	.359
#114							1	**.579****	**.648****	**.592****	**.615****	**.640****	**.637****	**.650****	**.623****	**.462***	**.670****	**.664****	**.645****	.229
#118								1	**.979****	**.830****	**.951****	**.955****	**.948****	**.932****	**.937****	**.693****	**.846****	**.853****	**.952****	**.392***
#123									1	**.867****	**.952****	**.957****	**.960****	**.955****	**.946****	**.726****	**.857****	**.880****	**.963****	**.424***
#126										1	**.790****	**.790****	**.837****	**.869****	**.824****	**.921****	**.757****	**.901****	**.794****	**.491****
#138											1	**.996****	**.979****	**.963****	**.980****	**.669****	**.927****	**.907****	**.990****	**.390***
#153												1	**.976****	**.956****	**.975****	**.664****	**.934****	**.902****	**.992****	**.378***
#156													1	**.986****	**.981****	**.707****	**.899****	**.930****	**.978****	.341
#157														1	**.983****	**.753****	**.876****	**.943****	**.962****	**.395***
#167															1	**.706****	**.895****	**.922****	**.973****	**.407***
#169																1	**.667****	**.826****	**.659****	**.535****
#180																	1	**.912****	**.927****	.359
#189																		1	**.899****	**.418***
∑PCBs																			1	.347

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 11. Spearman correlations between PCBs, $\sum_{18}$PCBs, and lipid content (%) in pine needles.

	#28	#52	#77	#81	#101	#105	#114	#118	#123	#126	#138	#153	#156	#157	#167	#169	#180	#189	∑PCBs	Lipid
#28	1	**.899****	**.645****	**.452***	**.801****	**.706****	**.657****	**.729****	**.591****	**.514****	**.741****	**.617****	**.678****	.322	**.848****	**.517****	**.628****	**.498****	**.962****	-.301
#52		1	**.485****	.251	**.799****	**.638****	**.580****	**.679****	**.514****	.325	**.662****	**.527****	**.613****	.180	**.685****	.339	**.547****	**.399***	**.918****	-.278
#77			1	**.666****	**.701****	**.881****	**.849****	**.822****	**.451***	**.696****	**.788****	**.381***	**.791****	**.565****	**.656****	**.542****	**.597****	**.672****	**.661****	-.299
#81				1	.327	**.540****	**.715****	**.509****	.304	**.742****	**.514****	.263	**.653****	.357	**.534****	**.544****	**.578****	**.558****	**.443***	-.068
#101					1	**.815****	**.646****	**.879****	**.522****	**.439***	**.860****	**.681****	**.744****	**.416***	**.655****	.324	**.632****	**.456***	**.871****	-.325
#105						1	**.857****	**.919****	**.467****	**.534****	**.868****	**.564****	**.825****	**.593****	**.713****	**.457***	**.673****	**.608****	**.772****	-.220
#114							1	**.817****	.360	**.649****	**.732****	**.420***	**.821****	**.614****	**.688****	**.542****	**.719****	**.765****	**.698****	-.290
#118								1	**.612****	**.540****	**.925****	**.703****	**.859****	**.578****	**.737****	**.434***	**.778****	**.555****	**.836****	**-.428***
#123									1	**.395***	**.510****	**.524****	**.424***	.253	**.495****	.236	.317	.152	**.640****	**-.396***
#126										1	**.539****	.267	**.625****	.306	**.488****	**.655****	**.526****	**.531****	**.485****	-.150
#138											1	**.758****	**.897****	**.573****	**.785****	**.511****	**.846****	**.570****	**.846****	**-.361***
#153												1	**.619****	**.440***	**.632****	.318	**.754****	.227	**.735****	-.309
#156													1	**.548****	**.698****	**.657****	**.864****	**.700****	**.774****	-.266
#157														1	**.452***	.343	**.469****	**.583****	**.382***	-.296
#167															1	**.607****	**.739****	**.645****	**.853****	-.349
#169																1	**.576****	**.598****	**.498****	-.141
#180																	1	**.569****	**.730****	-.315
#189																		1	**.507****	-.191
∑PCBs																			1	**-.382***

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

3.5.3 Correlations between PCDD/Fs, PCBs, and organic contents

The Spearman correlations between sum of PCDD/Fs, dl-PCBs, indicator PCBs (I-PCBs) and TOC in soils were determined by Spearman correlation analysis (Table 12). For soils, $\sum_{17}$PCDD/F levels had strong positive correlations with $\sum_{12}$PCBs ($r = 0.542$, $p < 0.01$) and $\sum_{7}$PCBs ($r = 0.544$, $p < 0.01$), meaning that they share common source areas, atmospheric transport/deposition pathways, and/or they are similarly retained by soil stores. The sum of dl-PCBs was significantly correlated to the sum of indicator PCBs due to their similar structures, and they also had positive correlations with TOC, indicating that TOC is the determining factor of dl-PCB concentrations in soils (Nam et al., 2008; Wang et al., 2008).

Table 12. Spearman correlations between sum of PCDD/Fs, dl-PCBs, and indicator PCBs, and TOC (%) in soils.

Soil	∑PCDD/Fs	∑dl-PCBs	∑I-PCBs	TOC
∑PCDD/Fs	1	**.542****	**.544****	.152
∑dl-PCBs		1	**.947****	**.400***
∑I-PCBs			1	.336

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Correlations between sum of PCDD/Fs, dl-PCBs, indicator PCBs, and lipid content in pine needles are shown in Table 13. Total concentrations of each organic pollutant were correlated with each other, because they tend to be polluted onto/into the pine needles following the similar translocation cycle in the atmosphere (Kurokawa et al., 1996). Unlike the correlation results in soils, $\sum_{17}$PCDD/Fs and $\sum_{7}$PCBs had no significant correlation except $\sum_{12}$PCBs levels ($r = -0.391$, $p < 0.05$), meaning that direct contamination and other physicochemical factors of the compounds (Log K_{oa}) would be the main reasons (Chun, 2009).

Table 13. Spearman correlations between sum of PCDD/Fs, dl-PCBs, and indicator PCBs, and lipid content (%) in pine needles.

Pine needle	∑PCDD/Fs	∑dl-PCBs	∑I-PCBs	Lipid content
∑PCDD/Fs	1	**.571****	**.600****	-.166
∑dl-PCBs		1	**.790****	**-.391***
∑I-PCBs			1	-.348

*Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

3.6 Physicochemical properties of PCDD/Fs and PCBs in media

3.6.1 Comparisons of PCDD/Fs between two media

To understand the physicochemical properties of two media, the PCA was carried out between target compounds and samples from sampling sites appeared in Figure 28. The PC 1 and PC 2 for the sampling sites accounted for 53% and 21% of the total variance, respectively. In the score plot, the soil and pine needle samples at each site were clearly separated based on their congener profiles previously mentioned in Figure 11. PC 1 was characterized by positive loadings of some hepta- to octa-CDF congeners and most hexa- to octa-CDD congeners, whereas PC 2 was characterized by positive loadings of tetra-to hepta-CDF congeners in the loading plot. The soil samples were clustered in the score plot with the loadings of higher chlorinated PCDD/Fs (hepta- to octa-CDFs and hexa- to hepta-CDDs), suggesting that the congeners with low volatility due to the high K_{oa} are more likely deposited to the terrestrial surfaces (Lohmann et al., 1998). On the other hand, the pine needle samples were grouped together in the score plot with the negative loadings of higher chlorinated furans (tetra-to hepta-CDFs), explaining that certain chlorinated compounds in vapor phases (tetra-CDFs) are absorbed by pine needles, while particulate ones (hepta- to octa-CD/Fs) are prone to adsorb to the particulate matter and washed off by rainfall from the surface of the leaves (Kurokawa et al., 1996; Ok et al., 2002; Rappolder et al., 2007).

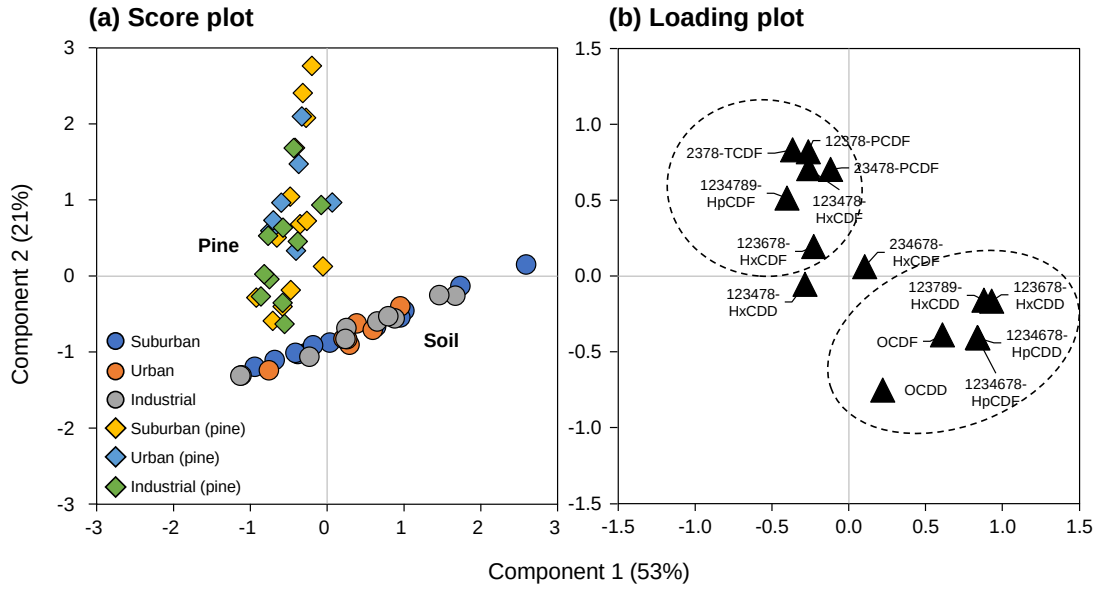

Figure 28. Principal component analysis results of PCDD/Fs in soils and pine needles. 2,3,7,8-TCDD, 1,2,3,7,8,9-HxCDF, and 1,2,3,7,8-PCDD were excluded due to their detection rate less than 50%.

3.6.2 Comparisons of PCBs between two media

The PCA was conducted to see the relationship between 18 PCB congeners and samples at sampling sites shown in Figure 29. The PC 1 and PC 2 for the sampling sites accounted for 43% and 24% of the total variance, respectively. Similar to the PCA results of PCDD/Fs, the soil and pine needle samples at each site were clearly separated based on their congener profiles previously mentioned in Figure 18 and 25. PC 1 was characterized by positive loadings of tetra- to hepta-CBs whereas PC 2 was characterized by positive loadings of tri- to hexa-CBs in the loading plot. The soil samples were a bit scattered in the score plot with the positive PC 1 loadings of higher chlorinated PCBs (penta- to hepta-CBs). The PCB homologues greater than penta-CBs have higher K_{oa}, which is easily deposited on the soil, water surface, and plants with less evaporation, leading to continuous deposition (Yeo et al., 2004). The pine needle samples in all areas were gathered on the left side of the score plot, with the negative PC 1 loadings of lower chlorinated PCBs (tri- to tetra-CBs). This phenomenon was well reported in the previous studies that the congeners in the gaseous phase tend to penetrate via stomata of the pine needles due to the low K_{ow} whereas higher chlorinated (penta-to hexa-) PCBs bound to particulate matters are likely adsorbed to the epicuticular wax surface for a short period (Baráková et al., 2017; Chen et al., 2006; Liu et al., 2020).

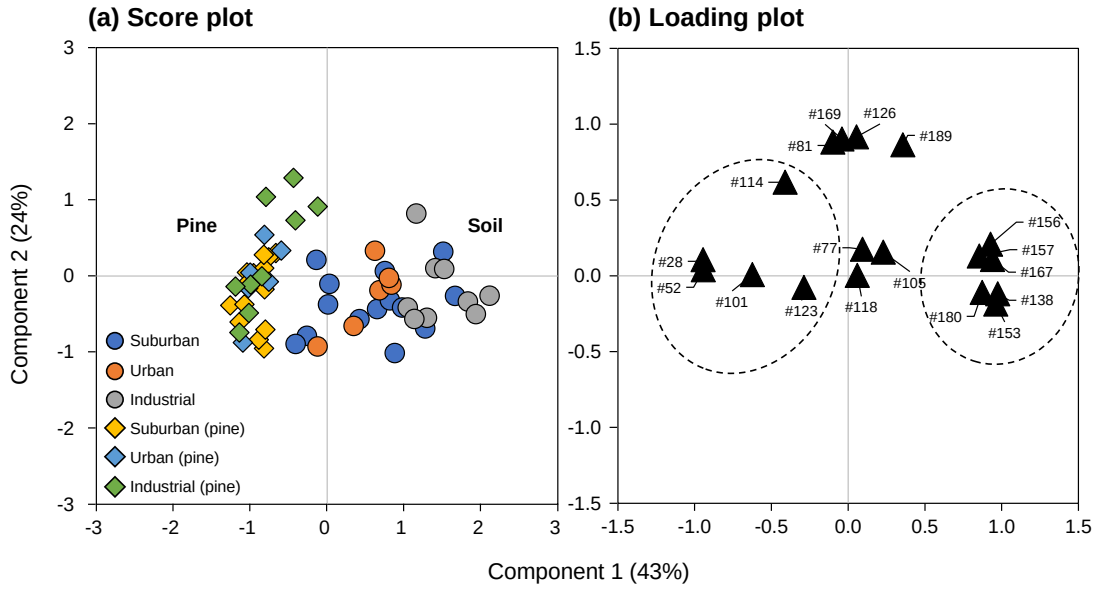

Figure 29. Principal component analysis results of 18 PCBs in soils and pine needles.

IV. CONCLUSIONS

This study identified the spatial distributions of PCDD/Fs and PCBs of two media, including soils and pine needles in Ulsan, Korea. From the total concentrations and spatial distributions for three areas, the industrial area had higher concentrations of PCDD/Fs, dl-PCBs, and indicator PCBs in soils than those from suburban and urban areas. Since Ulsan has the industrial complexes on a large scale, the concentrations of target compounds in soils were mainly influenced by the industrial processes. Soils in urban and suburban areas; however, had the similar levels of PCDD/Fs and PCBs, indicating that suburban area was affected to either from the local sources or from the urban and industrial areas. Pine needles in some industrial sites were primarily polluted, but other than that, those from three areas were not different owing to the atmospheric transport of PCDD/Fs and PCBs based on the physicochemical properties and meteorological conditions.

According to the results of average and individual profiles for sampling sites, the average composition of $\sum_7$PCDDs accounted for about 77% of the normalized concentrations in soils. The industrial area had a different profile compared to those of the urban and suburban areas, contributing slightly higher $\sum_{10}$PCDFs due to the industrial activities. Furan groups with higher chlorine atoms such as HxCDFs and HpCDFs were predominant about 82% of the normalized concentrations in pine needles. For dl-PCBs and indicator PCBs in soils, about 85%, 60% of penta- and hexa-CBs were accounted for the total normalized concentrations, respectively. In case of pine needles, on the other hand, about 87% of tetra- and penta-CBs, about 80% of tri- to penta-CBs were accounted for the normalized concentrations.

According to the results of Spearman correlation analysis, $\sum_{17}$PCDD/Fs and $\sum_{18}$PCBs were positively correlated with each other, representing that Ulsan has many pollution sources in common, such as incomplete combustions and usage of commercial products during the industrial processes. However, TOC and most PCDFs and heavy chlorinated PCBs (penta- to hepta-CBs) had positive correlations because of their strong binding tendency to the organic carbons in soil while PCDDs and light chlorinated PCBs (tri- to tetra-CBs) had no correlations, assuming that they are directly deposited on the soil layer regardless of its organic carbon content. With the respect of pine needles, the correlation between every PCDD/F and PCB congener was somewhat impossible due to the unstable state of deposition in pine needle for organic compounds owing to the various factors such as photodegradation and changes in temperature. Furthermore, the lipid content of pine needle and PCDD/F and PCB congeners had negative or no correlations, indicating that physicochemical factors of each congener such as K_{ow} and K_{oa} would be mainly affected the sorption of organic pollutants to the bioindicator. Eventually, it is imperative to study both media to understand the entire pathways of organic pollutants in the environment.

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SUPPLEMENTARY INFORMATION

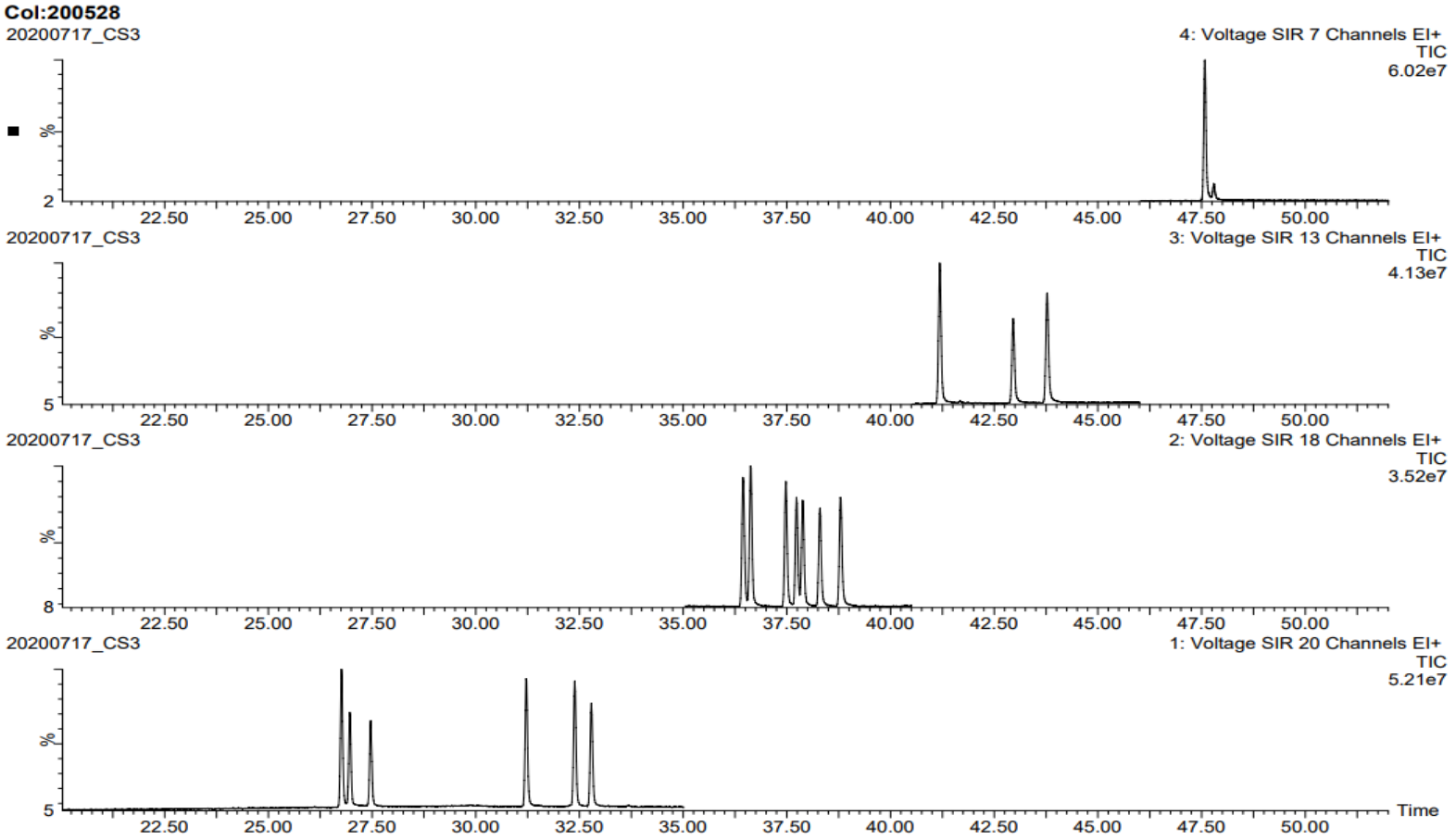

Figure S1. Chromatogram of PCDD/F standard.

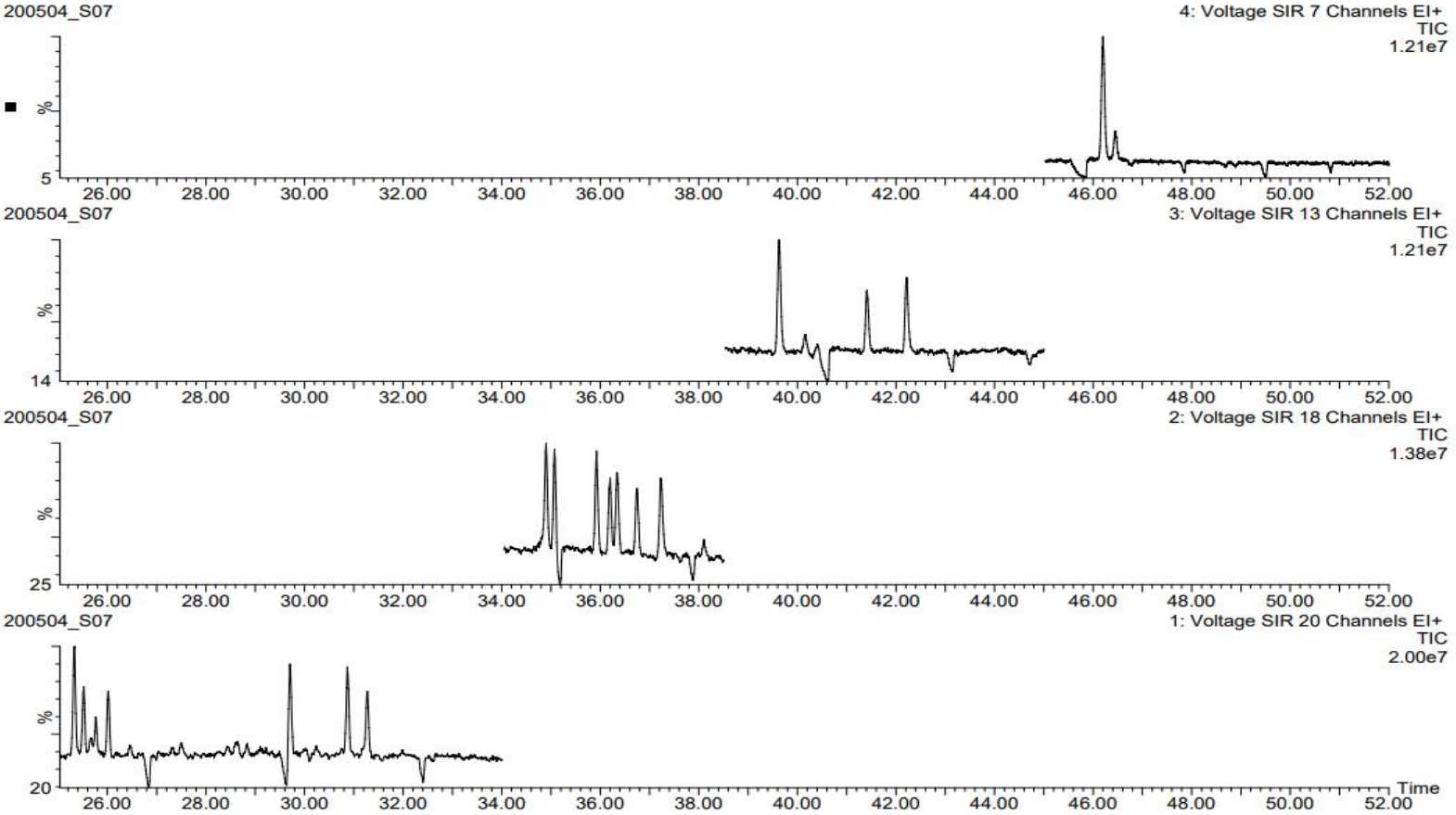

Figure S2. Chromatogram of PCDD/Fs in sample.

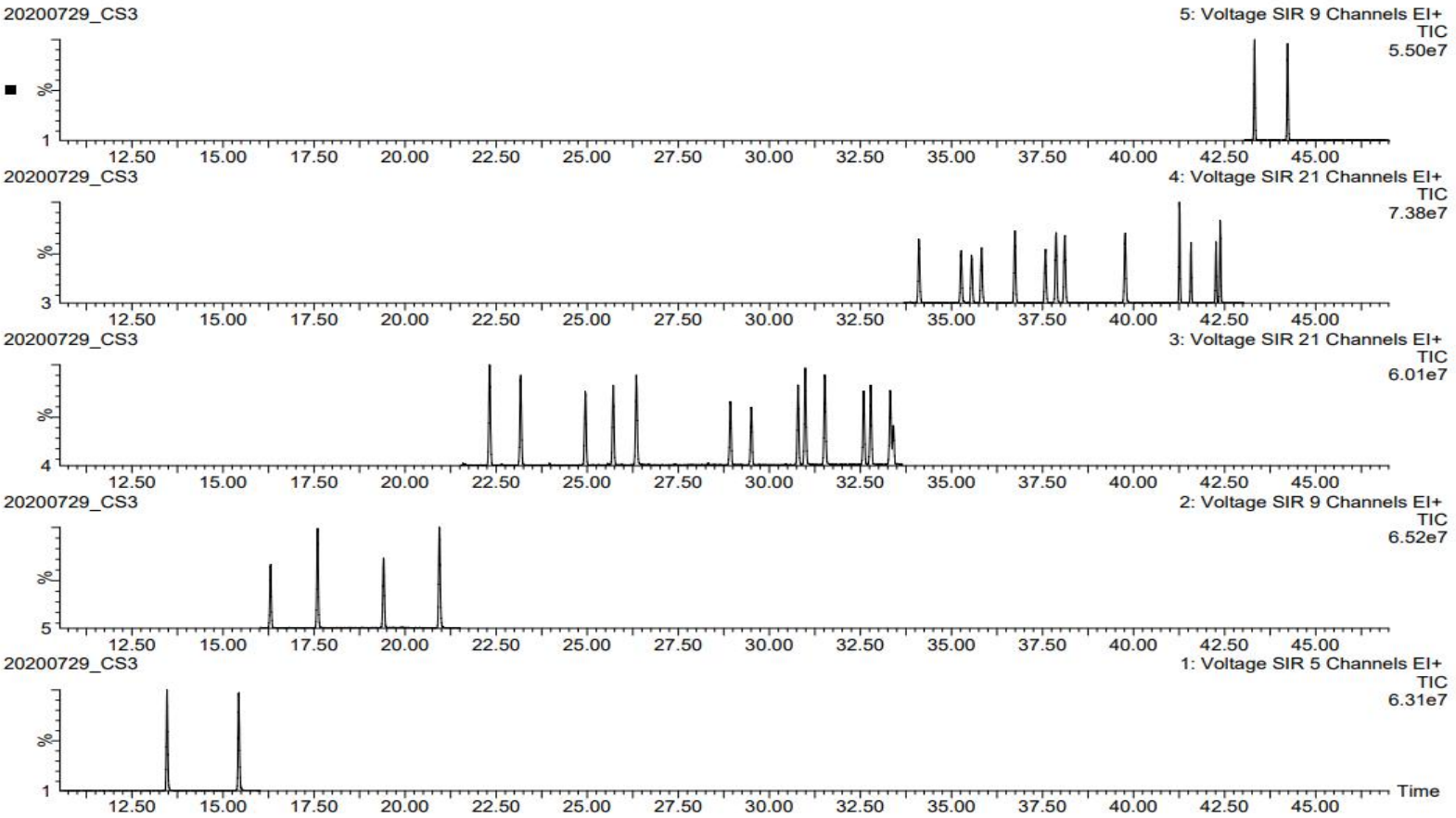

Figure S3. Chromatogram of dl-PCB standard.

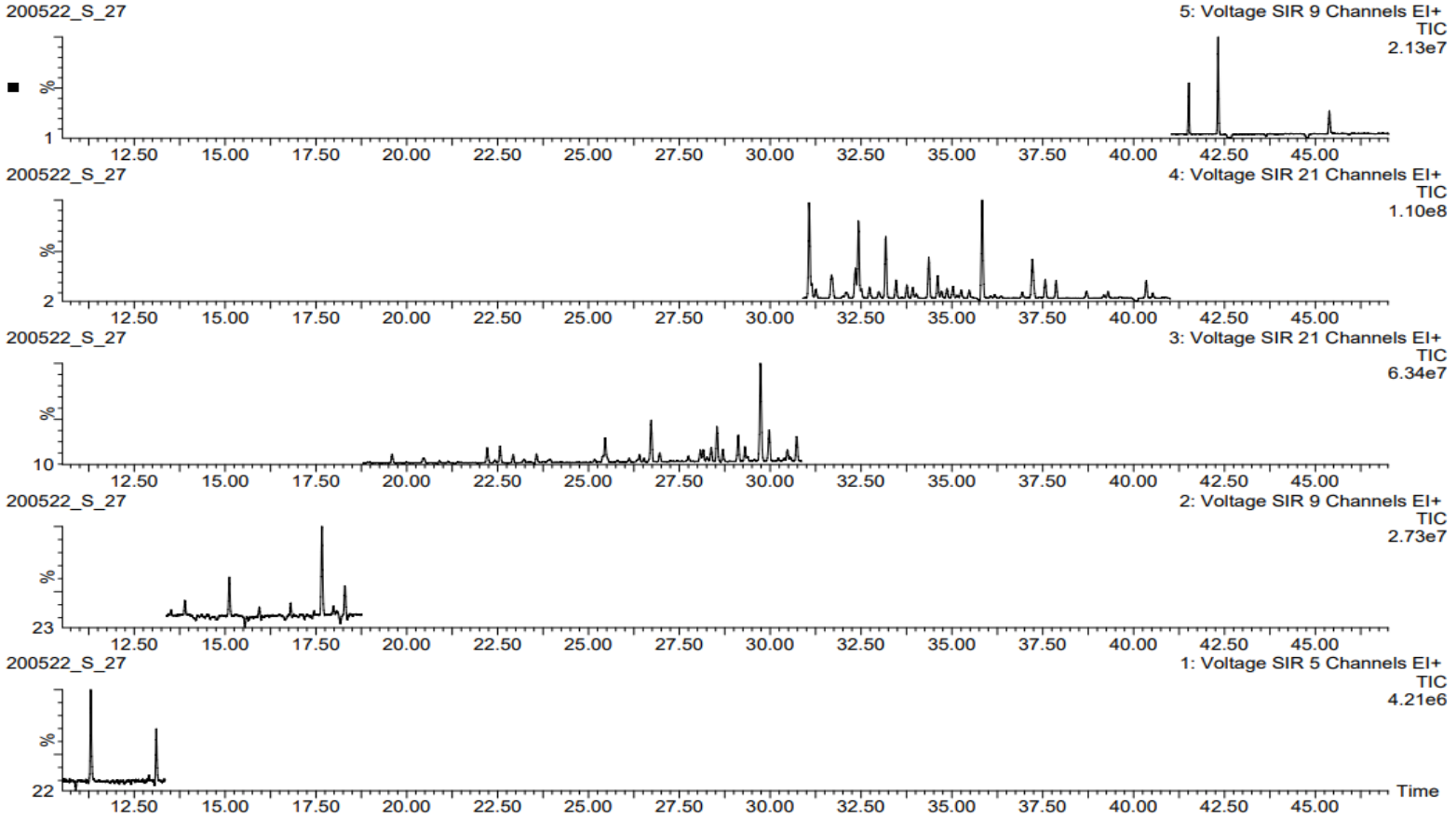

Figure S4. Chromatogram of dl -PCBs in sample.

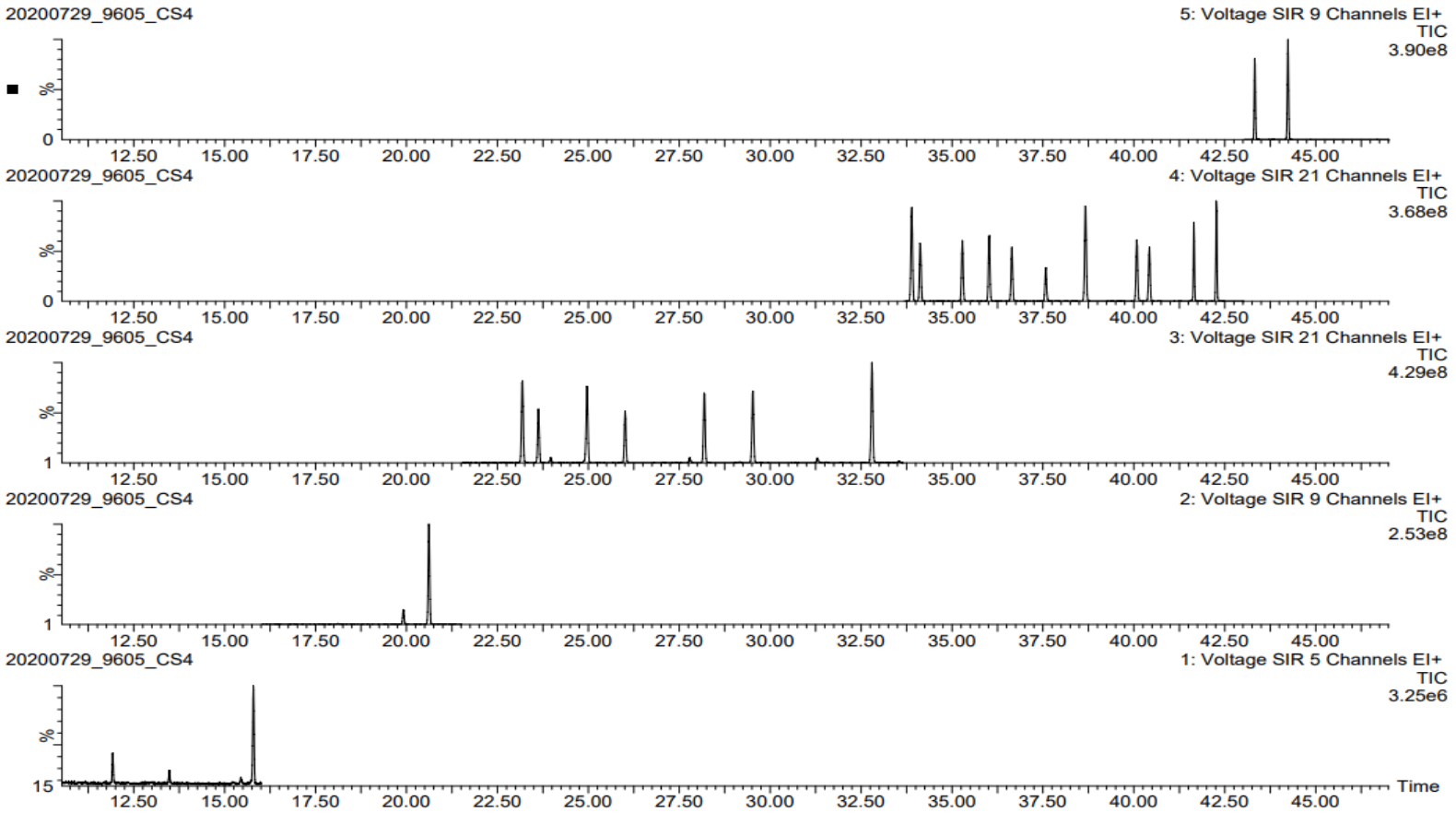

Figure S5. Chromatogram of indicator PCB standard.

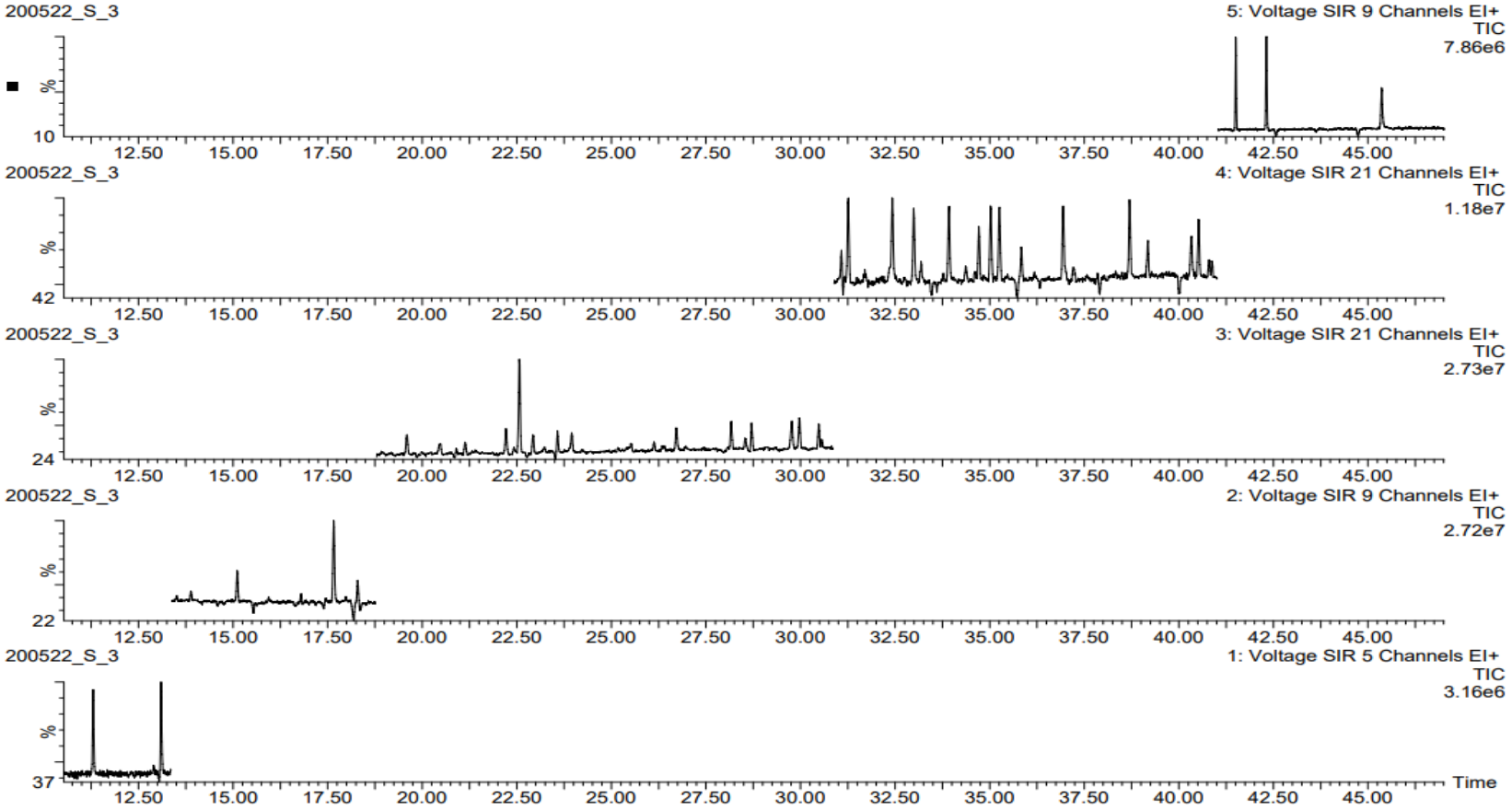

Figure S6. Chromatogram of indicator PCBs in sample.

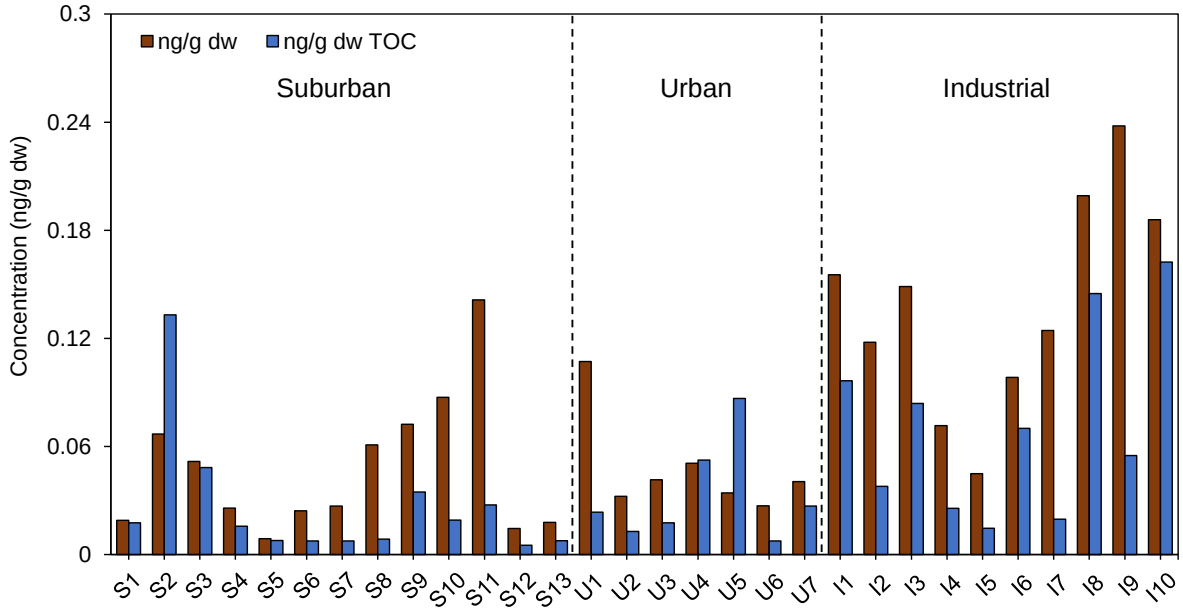

Figure S7. TOC-normalized concentrations of PCDD/Fs in soil samples.

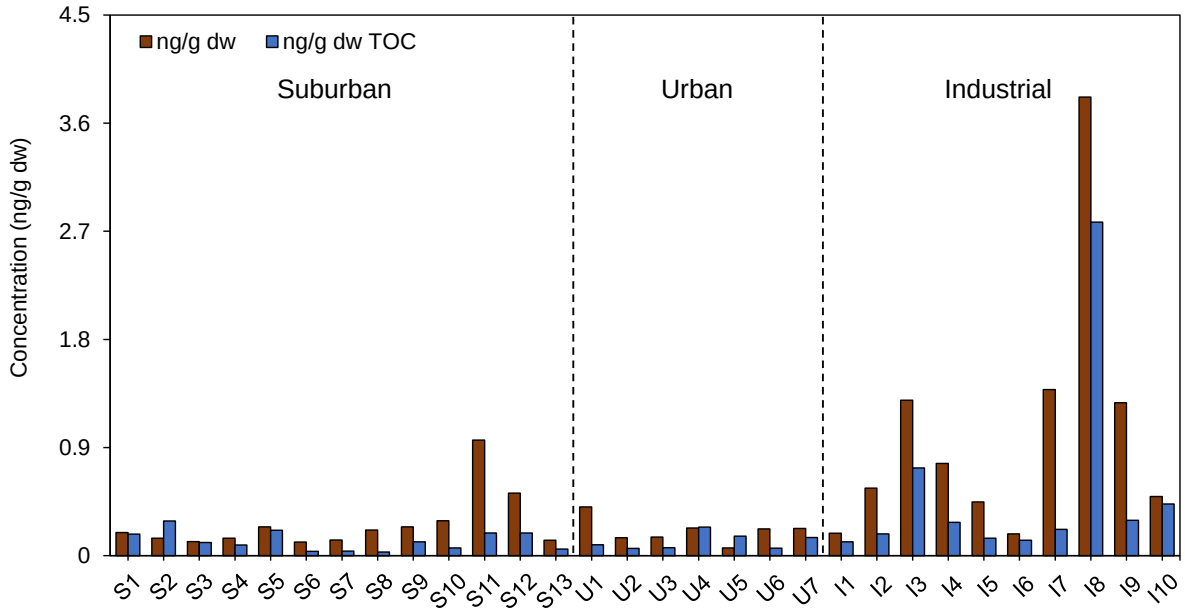

Figure S8. TOC-normalized concentrations of PCBs in soil samples.

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먼저, EACL 연구실에 권유해주신 최성득 교수님께 감사의 뜻을 표합니다. 대학원 생활을 하면서 환경분석화학의 기본적인 지식을 바탕으로 다양한 연구를 접하게 해준 교수님께 진심으로 감사합니다. 학부 전공이 다름에도 불구하고 환경 분석 분야에 관심을 가질 수 있었던 좋은 발판이 되었습니다.

졸업 논문 발표에 피드백을 주신 송창근 교수님과 박상서 교수님께 감사드립니다. 조언 내용을 바탕으로 학위 논문을 좀 더 구체적으로 보완할 수 있었습니다.

석사과정을 하면서 같이 지냈던 EACL 연구실 분들께 감사의 마음을 전합니다. 연구실에서 처음 올 때부터 졸업 전까지 저를 잘 가르쳐 주시고 멘토가 되어 주셨던 민규 오빠, 성준 오빠, 진우 오빠, 실험하면서 많은 도움과 조언을 아낌없이 주셨던 지민 선생님, 누구보다 열정적이고 연구에 관련된 필요한 조언을 스스럼없이 주었던 상진, 호영, 인규, 석사 과정을 함께 하며 서로 응원하고 지지했던 근우, 혜지, 졸업했지만 연구에 관련된 도움을 많이 주었던 지영, 현진, 단비, 나라, 학위 논문 내용에 도움을 주었던 Nam 박사님, 과제 실험을 같이 했던 Quang, Renato, Tien, 그리고 새로 들어올 예비 대학원생들 민재, 종현, 그리고 남규까지 함께 지내면서 값지고 좋은 추억들을 안고 갈 수 있었습니다.

UCRF 분석센터에 계신 선생님들께도 감사합니다. 과제 실험과 제 실험에 많은 도움과 조언을 주셨던 이윤세 선생님, 예진 선생님, 손희식 선생님, 권도규 선생님, 그리고 실험 분석과 분석 결과에 대한 세세한 설명을 해주셨던 김철수 선생님 덕분에 학위 논문을 잘 쓸 수 있었습니다.

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